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Subject:

Post Mortem Analysis of Catalysts from Canadian Vehicles Fueled with MMT-containing Gasoline.

SUMMARY

A series of catalysts taken from Ford of Canada employee vehicles have been physically and chemically characterized to determine the effects of the fuel additive MMT. The results indicate the the combustion product of MMT,  $\rm Mn_3O_4$ , is the primary cause for the decreased efficiency of the catalysts. A 5 to 80 micron thick layer of  $\rm Mn_3O_4$  covers the washcoat and contributes to the deterioration of the catalyst efficiency. This layer in effect increases the mass transfer resistance and thus decreases the efficiency of the catalyst for converting HC and to lesser degrees,  $\rm NO_x$  and CO. Analytical results show that the inlets of the catalysts have between 0.7 and 3.0 wt% Mn while contaminants such as Pb, P, Zn and S are presnet at lower concentrations and do not contribute significantly to the deactivation of the catalysts. The analytical data also shows that as mileage increases the amount of manganese also increases.

Results and Discussions

Catalysts from 10 Ford of Canada Employee vehicles (11 catalysts) were removed from their respective vehicles and submitted to Research for comprehensive chemical and physical characterization. These vehicles were randomly selected and had  $\underline{no}$  reported mechanical or operational problems. These

vehicles were 1987-1989 3.0L/3.8L Taurus/Sables having in-use mileages between 21,500 miles and 62,224 miles (Table 1). Each vehicle had been fueled with commercially available Canadian fuel presumably containing the fuel additive MMT at a concentration of 1/16 g Mn/gal, as allowed by Canadian law.

Table 1
Canadian Vehicles

<u>Number</u>	<u>Vehicle</u>	<u>MY</u>	<u>Engine</u>	Mileage
BK1	Taurus	1988	3.0L	35,733
BK2	Sable	1989	3.0L	28,840
BK3	Sable	1988	3.0L	44,235
BK4	Taurus	1988	3.0L	41,093
BK5	Sable	1988	3.0L	21,500
BK6	Taurus	1987	3.0L	48,174
BK7A*	Sable	1988	3.8L	62,224
BK7B*	Sable	1988	3.8L	62,224
BK8	Taurus	1987	3.0L	33,354
BK9	Sable	1988	3.0L	27,416
BK10	Taurus	1988	3.0L	39,662

BK7A and BK7B refer to the 2 brick system on the 3.8L Engine class, right and left side (driver side), respectively

The as-received condition of each individual catalysts used in this evaluation are shown by the photographs contained in appendices A-J of this report. Visually, the interior of the converter housings were coated with a rust colored residual deposit. Further visual inspection of the ceramic monoliths also showed the outside and channels to be coated to varying degrees with the rust colored deposit. The inlets of the monoliths showed the heaviest amounts of the rust colored residue. Similarily, the outlets of the monoliths also exhibited the rust colored residue but to a lesser degree. X-Ray diffraction analysis of the deposit indicate it to be Mn<sub>3</sub>O<sub>4</sub>. Clogging of several of the channels were observed in samples BK1 (35,733 miles) and BK7A-7B (62,224 miles). None of the monoliths showed visual signs of exposure to abnormally high operating temperatures.

The results of x-ray fluorescence analysis of samples taken from each individual monolith are detailed in appendices A-J. A summary of the major contaminants along with the B.E.T. surface area values are shown in Table 2. Manganese concentrations, as expected, are highest at the inlet of the monoliths and decrease toward the outlet. Manganese concentration at the inlets ranged from a low of 0.79 wt% to a high of 3.23 wt%. This data is graphically summarized in figure 1 and shows that as mileage increases the concentration of Mn also increases. It is important to note that other contaminants such as Pb, S, P, and Zn are all within normal ranges for these levels of accumulated in-use mileage.

Optical micrographs of each of the catalysts are shown in appendices A-J. The inlet channels of the monoliths have a layer of residue varying in thickness covering the washcoat. Based on the optical micrographs at 80X, estimates of the thickness vary from approximately 5 microns on the ribs to approximately 30 microns on the filet area of the monoliths. In some cases the thickness of the layer is estimated at 10 times greater than the washcoat thickness.

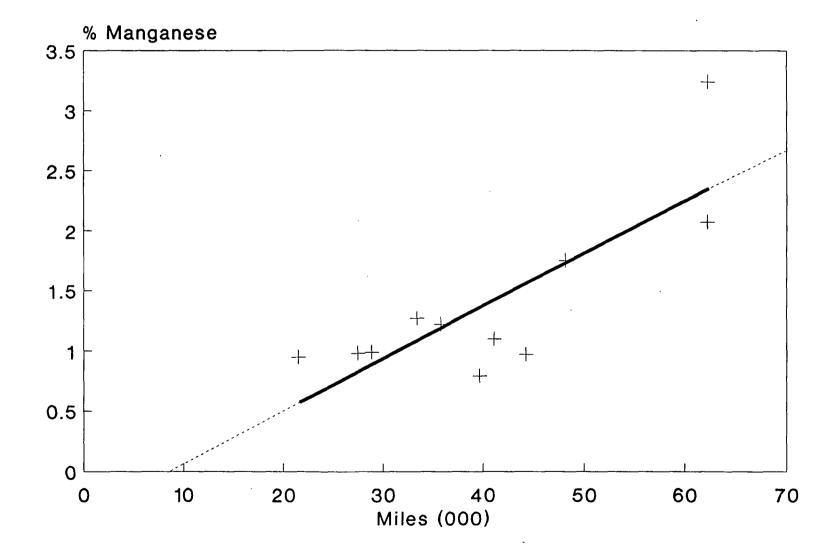


Figure 1- X-ray Fluorescence Analysis of Catalyst versus Vehicle Mileage

Number	Vehicle	<u>MY</u>	Mileage	<u>Mn</u>	<u>Pb</u>	<u> </u>	<u> </u>	<u>Zn</u>	B.E.T. Area, m <sub>2</sub> /g
BK1	Taurus	88	35,733	1.22	. 20	.06	.13	.15	19.1
BK2	Sable	89	28,840	0.99	.14	0	.13	. 08	19.0
BK3	Sable	88	44,235	0.97	.18	. 02	. 18	.13	19.0
BK4	Taurus	88	41,093	1.10	.08	0	.13	. 07	19.0
BK5	Sable	88	21,500	0.95	. 04	. 04	.10	.05	14.3
BK6	Taurus	87	48,174	1.74	.13	.07	.12	.09	18.0
BK7A*	Sable	88	62,224	2.07	.18	0	.21	.21	19.7
BK7B*	Sable	88	62,224	3.23	.16	0	. 26	. 30	12.0
BK8	Taurus	87	53,354	1.27	. 22	. 06	.16	.11	17.0
вк9	Sable	88	27,416	0.98	.12	0	.21	.15	19.0
BK10	Taurus	88	39,662	0.79	.13	.13	.08	.09	19.3

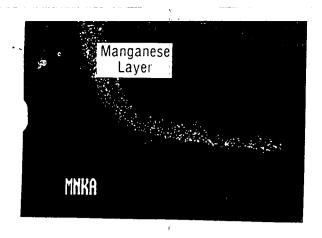
<sup>\*7</sup>A and 7B refer to driver side and passenger side catalysts, respectively on 3.8L catalysts engine system.

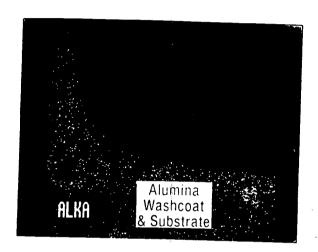
Scanning electron microscopy and electron microprobe analysis were used to identify and more precisely measure the thickness of the Mn layer. Shown in Figure 2 are typical secondary electron images and elemental maps of two of the samples. Using these elemental maps one can measure the thickness in the filet area to be 60 microns as compared to the washcoat of approximately 30 microns. Exact measurements of the thickness using electron microprobe linear transverse spectrum analysis (elemental line scans) indicate that the thickness may vary from a low of 17 microns on a rib areas to a high of 81 microns in the filet area of the monolith. These electron microprobe line scans are shown in appendices 6 and 7 for samples BK6 (48,174 miles) and BK7 (62,224 miles).

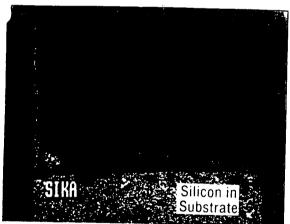
Average B.E.T. surface areas range between 12.0 and 19.0  $\rm m^2/g$  for the catalysts examined in this evaluation (Table 2). The B.E.T. values for inlet, middle, and outlet samples are also given in appendices A-J of this report. This data confirms visual observations that the catalysts were not exposed to abnormally high operating temperatures and were not thermally stressed prior to removal from the vehicle. Fresh catalysts generally exhibit B.E.T. values of approximately 25  $\rm m^2/g$  whereas an aged catalyst could have a B.E.T value as low as 5  $\rm m^2/g$  and still retain considerable catalytic activity. The lowest value of 12  $\rm m^2/g$  was observed for the 62,224 miles vehicle and this is not considered to be outside of the normal range for vehicles with this mileage accumulation.

Laboratory measurements of conversion efficiencies and lightoff characteristics were obtained for each of the catalysts using synthetic exhaust gas mixtures. The steady state and light-off curves for each individual sample are given in appendices A-J. The HC efficiencies are summarized in figures 3-5. In these figures percent HC efficiency is plotted against R values (redox ratio). The redox ratio, is a measure of the exhaust stoichiometry and is related to the A/F ratio. An R > 1 indicates a net excess of reducing species (CO and HC) and R < 1 indicates a net excess of oxidizing species (NO and  $O_2$ ). Included in this summary for comparison is data from a catalyst obtained from a non-MMT fueled vehicle of comparable mileage, model and year. The data show that HC efficiency is significantly reduced in those catalysts that have been exposed to the fuel additive MMT when compared to those catalysts from a vehicle operated without MMT in the fuel. Figure 6 shows similar HC efficiency curves for outlet portions from the catalysts used in this study. In those cases where the Mn concentration is low (approximately 0.3 wt%), the efficiencies compare favorably with the catalyst from the non-MMT fueled vehicle. In the case of the high mileage MMT fueled vehicle (62,224 miles) which has approximately 0.9  $\pi$ t% Mn, and the decrease in HC efficiency is significant at R = 1, indicates that Mn has a pronounced effect on catalyst activity at concentrations as low as 1 wt%.

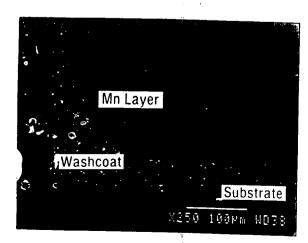
The EGO sensors taken from each of the vehicles were submitted to ELD (Electronics Division's sensors group) and to the Robert Bosch Company for more detailed analysis. The results show that each was coated with a layer of Mn and that each was functioning. However, the EGO from vehicles BK7 (62,224 miles) and BK9 (27,416 miles) exhibited some abnormal behavior but were still classified as being within specifications for functioning EGOs.



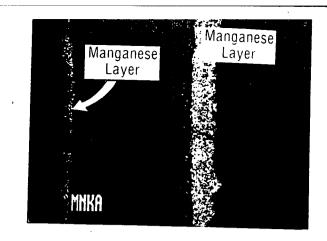


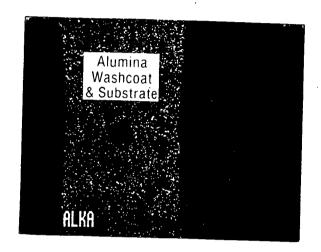


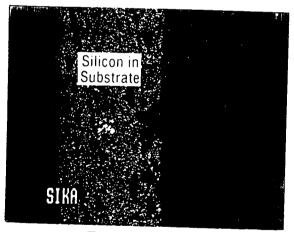
Elemental Maps



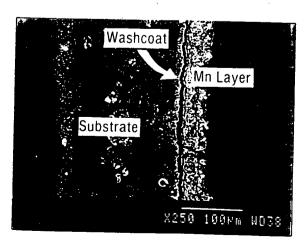
Secondary Electron Image Of Fillet Area







Elemental Maps



Secondry Electron Image Of Rib Area

% HC Conversion

62,224B MMT

120

Figure 3- HC Efficiencies of Inlet Samples versus Redox Ratio

41,115 NON MMT

 $\infty$ 

Figure 4- HC Efficiencies of Inlet Samples versus Redox Ratio

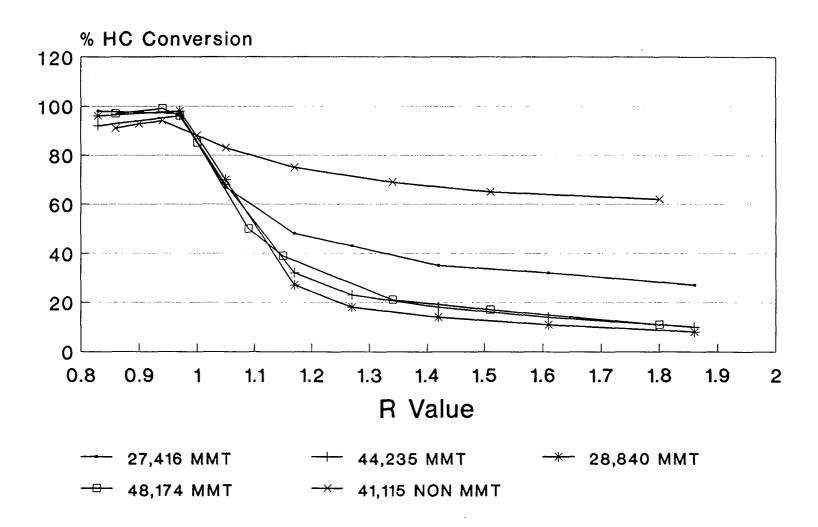
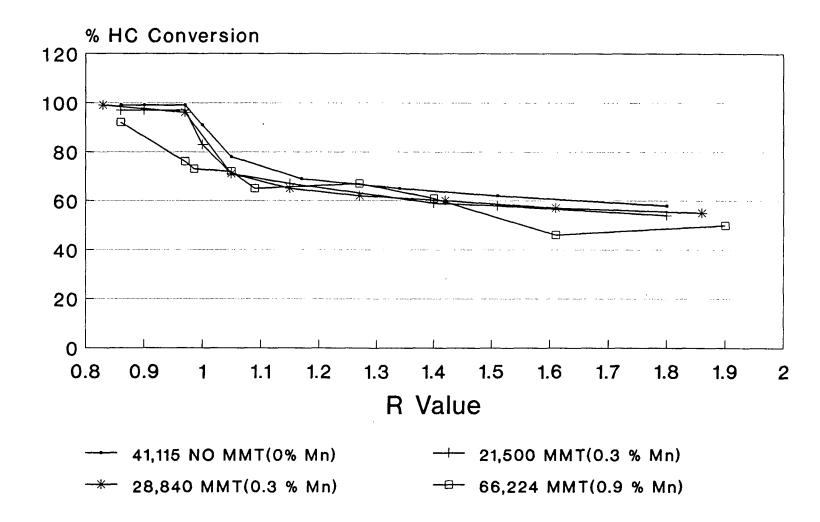


Figure 5- HC Efficiencies of Inlet Samples versus Redox Ratio



Samples from Outlet Portion

Figure 6- HC Efficiencies of Outlet Samples versus Redox Ratio

Summary

In summary, the efficiency of catalyst exposed to the fuel additive MMT (1/16 g Mn/gal) is significantly reduced. The data obtained from this set of catalysts taken from vehicles which were employee driven and had experienced no operational problems confirms those conclusions drawn from earlier data that the combustion product of MMT,  $\mathrm{Mn_3O_4}$ , does affect significantly the efficiency of the catalyst. This data shows conclusively that the  $\mathrm{Mn_3O_4}$  layer which begins to build even in low mileage vehicles adversely affects the ability of the catalyst to convert HC and  $\mathrm{NO_x}$  in a synthetic exhaust stream. The mechanism for this reduced efficiency is probably increased mass transfer resistance caused by the layer of  $\mathrm{Mn_3O_4}$  covering the washcoat. In this mechanism, the exhaust gases must penetrate a thick layer of  $\mathrm{Mn_3O_4}$  before they can reach the catalytically active sites on the washcoat. Consequently, this rate inhibiting step results in the reduced catalytic activity observed in this series of samples.

Concur:

H. S. Gandhi

R. G. Hurley

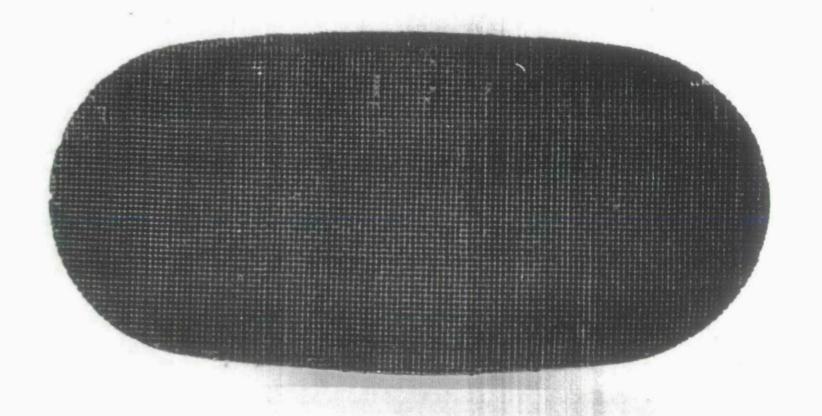
Contributors to the data in this report included: L. A. Hansen, D. Lewis, W. L. H. Watkins, C. Marry from the Chemical Engineering Department-Research; F. Kunz, R. Belitz, K. Plummer, R. Warsinski, F. Alberts from the Analytical Sciences Department-Research; and G. Beaudoin from ELD.

Appendix A 1988 3.0L Taurus 35,733 Miles

## X-RAY FLUORESCENCE ANALYSIS OF MMT CATALYSTS

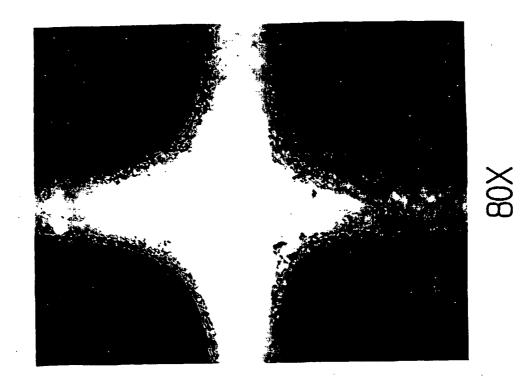
VEHICLE	B.E.T. AREA		nalysis TIC COM	(wt%)	<u> </u>						
CATALYST	$(m^2/g)$	PT	RH	PD	NI	CE	BA	LA	FE	g/ft <sup>3</sup>	Pt/Pd/Rh
1989 3.0L Tau	ırus	35,733	Miles		. <del></del>		<del></del>		<del></del>		
MMT-BK1I	20.6	. 1979	.0411	.0000	.7654	6.1937	. 8242	. 2404	. 3553	34.9	4.8/0/1.0
MMT-BK1M	18.9	.1705	.0355	.0000	.6886	6.2911	.7281	. 2422	. 3237	30.1	4.8/0/1.0
MMT-BK10	17.8	.1659	.0341	.0000	.6491	6.1441	. 6509	. 2391	. 3399	29.2	4.9/0/1.0
									Average:	31.4	4.8/0/1.0

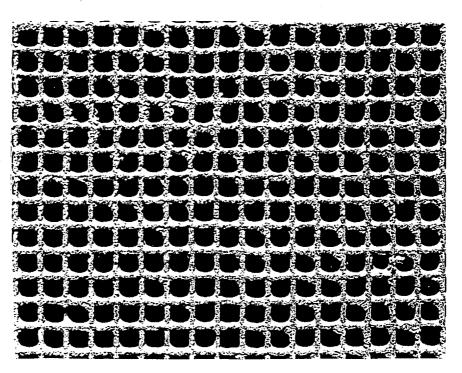
VEHICLE	CONTAMINATES									
CATALYST	PB	S	P	ZN	MN	CA	CL	CU		
MMT-BK1I	.2031	.0642	.1269	.1534	1.2169	.0604	.0000	.0254		
MMT-BK1M	.0722	.0000	.0749	. 0447	. 7475	.0195	.0000	.0227		
MMT-BK10	.0458	.0049	.0648	.0326	.6938	. 0327	.0000	.0202		



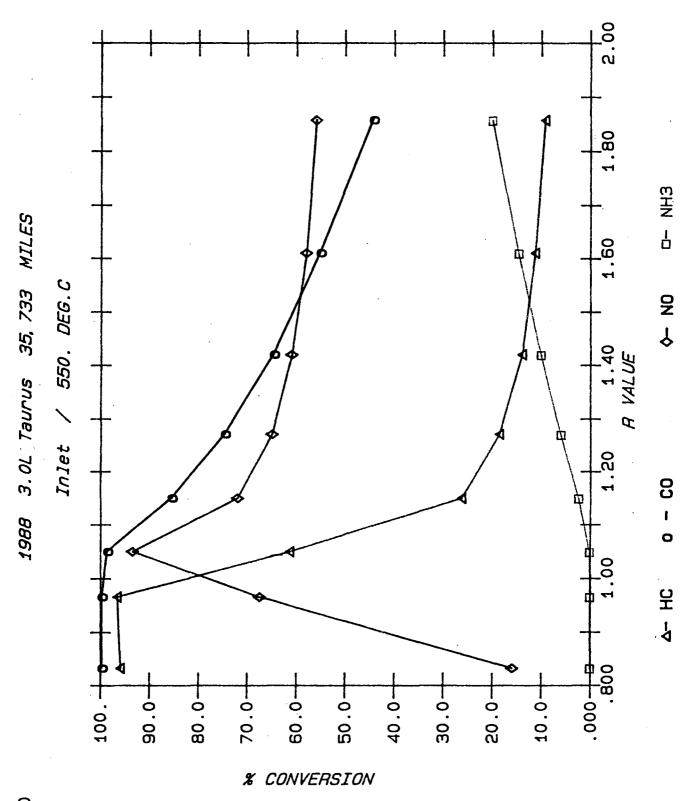
1988 TAURUS 3.0L ENGINE 35,733 MILES

1988 3.0L Taurus- 35,733 Miles Inlet



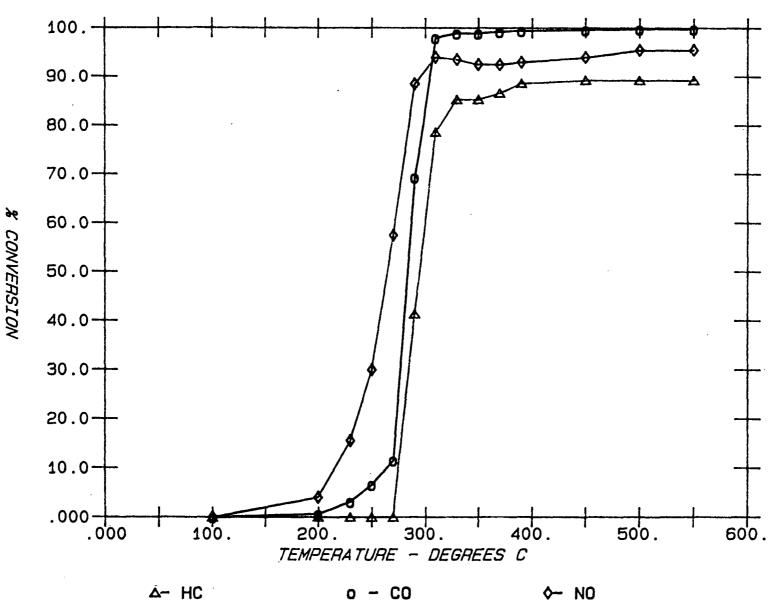






xE 





27

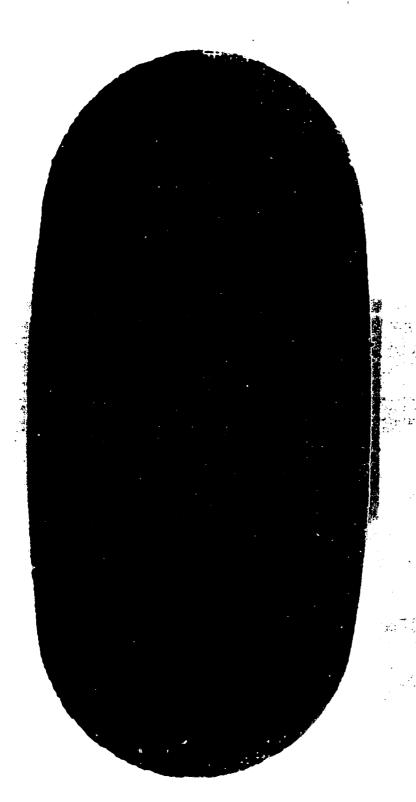
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Appendix B 1989 3.0L Sable 28,840 Miles

MMT-BK2I MMT-BK2M MMT-BK2O

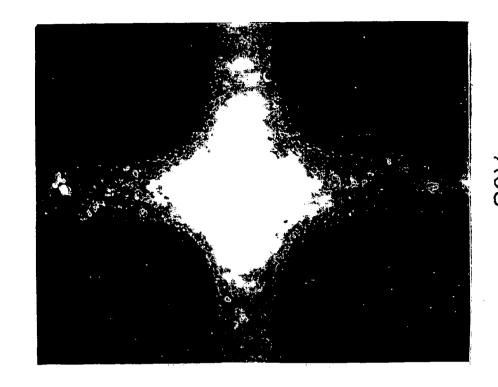
VEHICLE CATALYST	B.E.T.	XRF A	nalysis TIC COM	(wt%)	S						
	(m <sup>2</sup> /g)	PT	RH	PD	NI	CE	BA	LA	FE	g/ft <sup>3</sup>	Pt/Pd/Rh
MMT-BK2M 19	19.5 19.9 17.4	28,840 . 2058 . 1861 . 1779	Miles .0438 .0408 .0372	.0000 .0000 .0000	.7135	5.0654 5.3654 5.1285	.6672 .6184 .5896	.1975 .2052 .1987	.3525 .3491 .3523 Average:	36.4 33.1 31.4 33.6	4.7/0/1.0 4.6/0/1.0 4.8/0/1.0
VEHICLE CATALYST		CONTAM	NATES								

	TIMILED						
PB	S	P	ZN	MN	CA	CL	CU
.1393 .0369 .0219	.0000 .0000 .0000	.1284 .0499 .0353	.0756 .0114 .0096	.9894 .4615 .3313	.0374 .0165 .0152	.0000	.0248 .0198 .0222

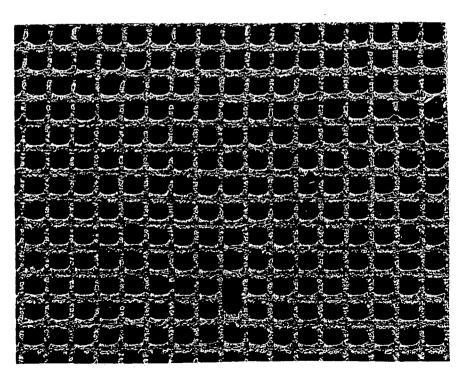


1989 SABLE 3.0L ENGINE 28,840 MILES

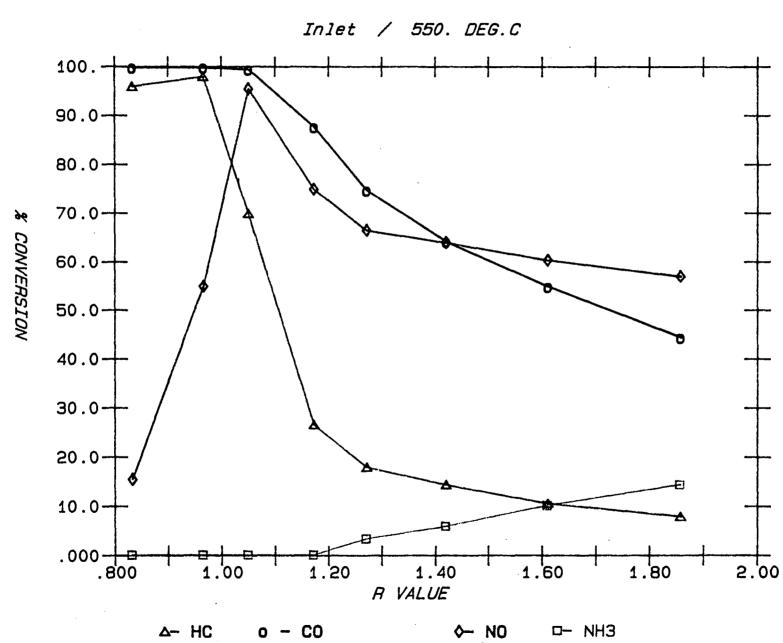
1989 3.0L Sable- 28,840 Miles Inlet



80X

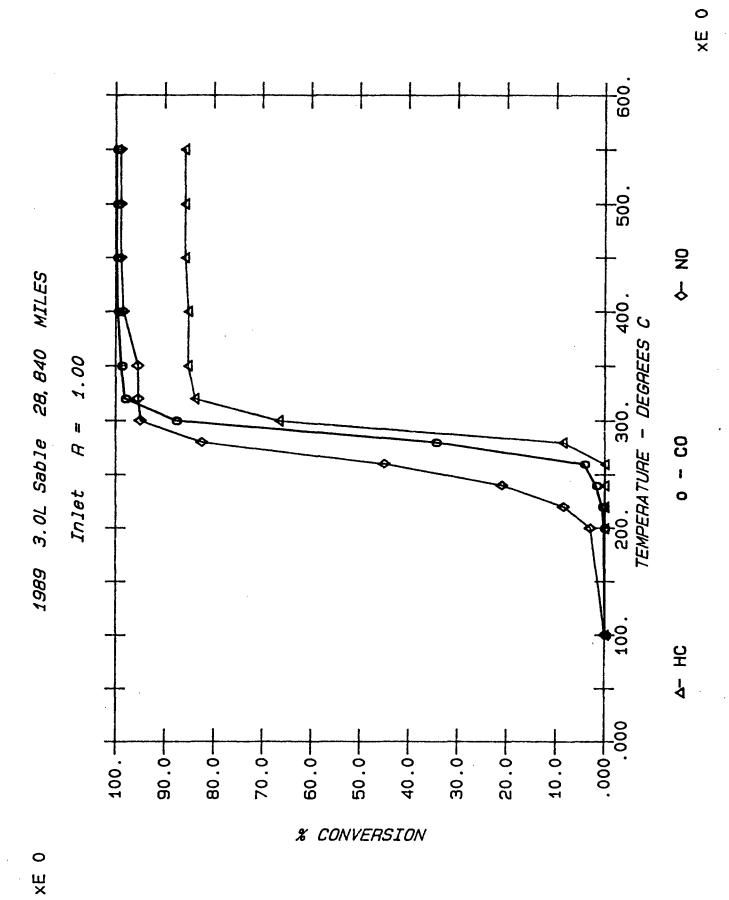


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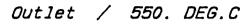


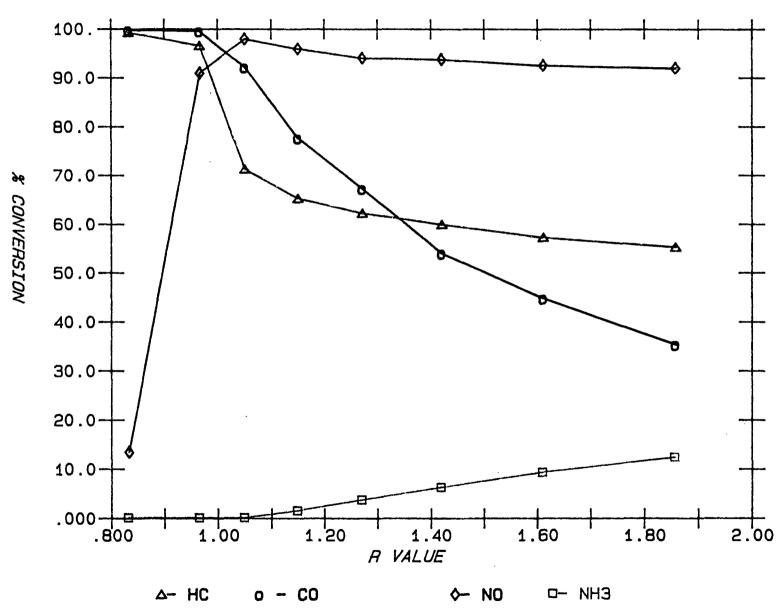
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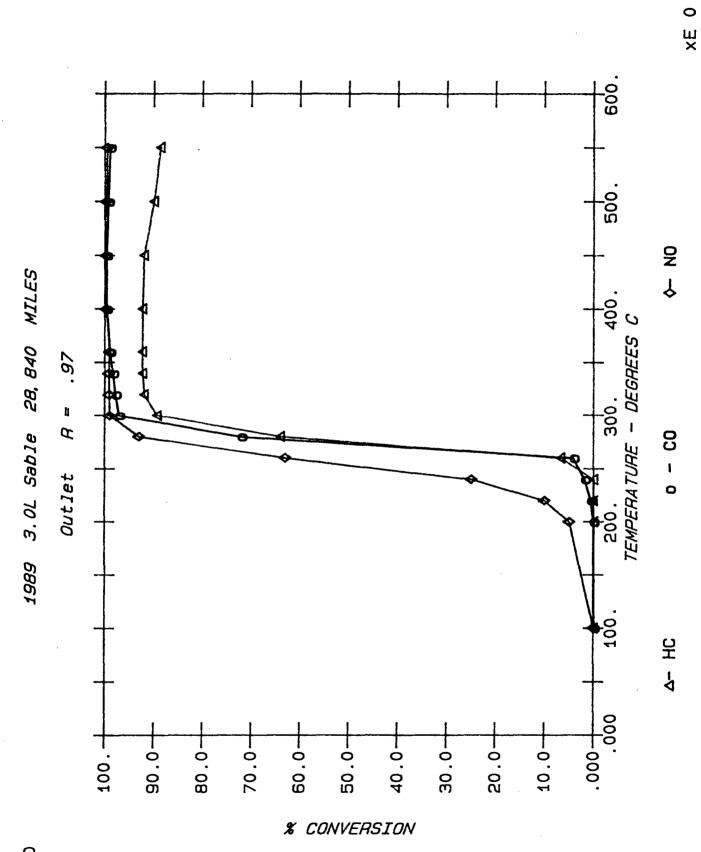
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xE 0



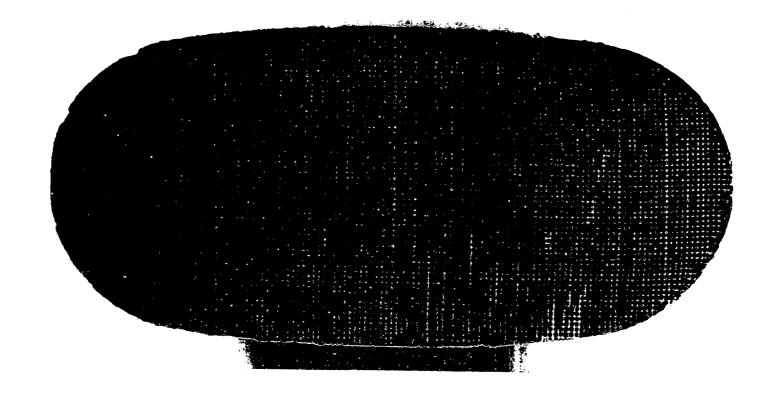


Appendix C 1988 3.0L Sable 44,235 Miles

## X-RAY FLUORESCENCE ANALYSIS OF MMT CATALYSTS

VEHICLE	B.E.T. XRF Analysis (wt%) AREA CATALYTIC COMPONENTS										
CATALYST	$(m^2/g)$	PT	RH	PD	NI	CE	ВА	LA	FE	g/ft <sup>3</sup>	Pt/Pd/Rh
1988 3.0L Sable		44,235	Miles								
MMT-BK3I	21.2	.1024	.0227	.0000	.7512	6.0490	.6420	.1715	. 3933	18.3	4.5/0/1.0
MMT-BK3M	16.6	.1040	.0235	.0000	.7059	5.8953	. 6835	.1698	. 3740	18.6	4.4/0/1.0
MMT-BK30	18.5	.0927	.0223	.0000	.6497	5.5785	.6124	.1597	. 3846	16.8	4.2/0/1.0
									Average:	17.9	4.4/0/1.0

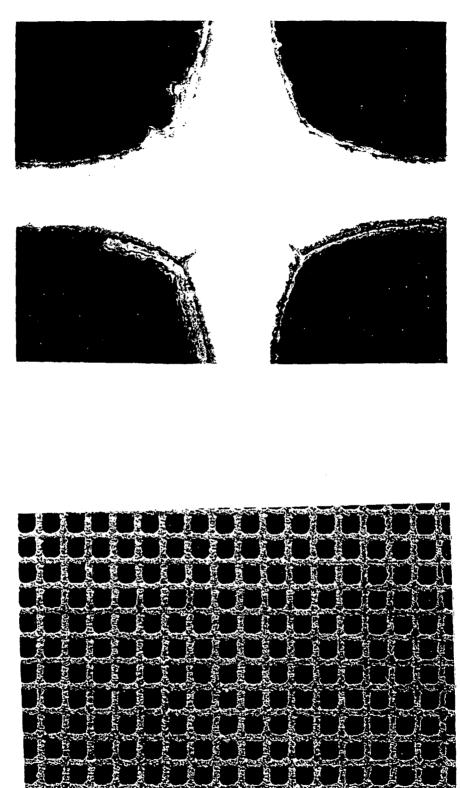
	CONTAMINATES									
VEHICLE CATALYST	PB	S	P	ZN	MN	CA	CL	cu		
MMT-BK3I	.1784	.0235	.1782	.1329	. 9651	.0449	.0000	.0282		
MMT-BK3M	.0626	.0000	.0943	.0349	.6066	.0328	.0000	.0234		
MMT-BK30	.0480	.0000	.0739	.0209	.4640	.0329	.0000	.0239		



1988 Sable 3.0L Engine 44,235 Miles

1988 3.0L Sable- 44,235 Miles Inlet

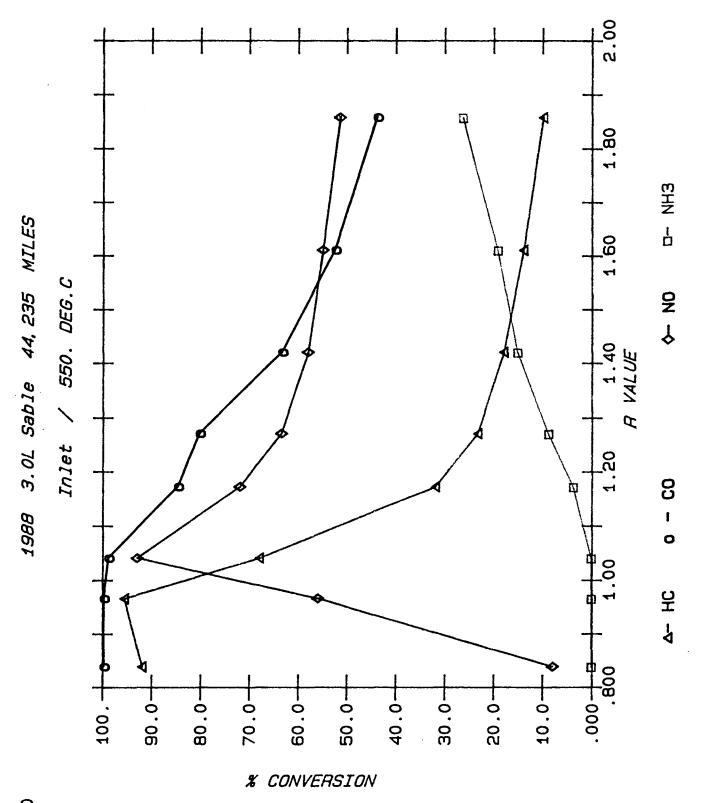




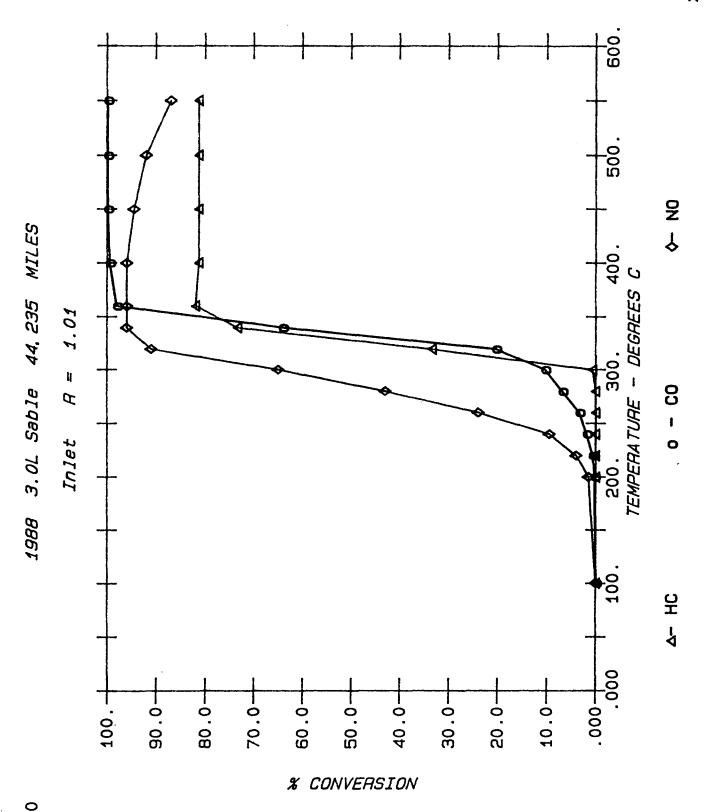
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80X





XE O



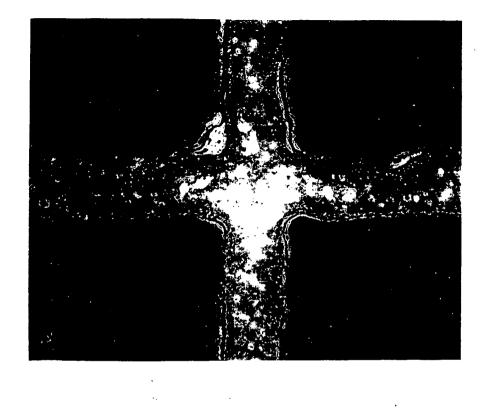
Appendix D 1988 3.0L Taurus 41,093 Miles

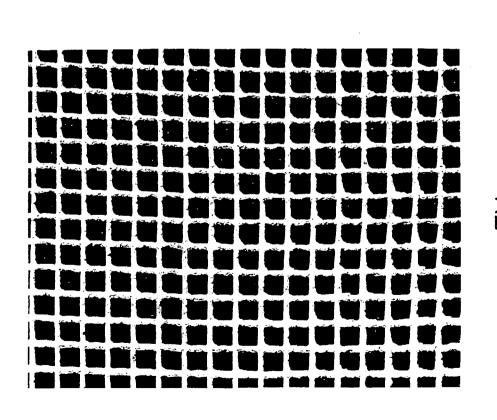
## X-RAY FLUORESCENCE ANALYSIS OF MMT CATALYSTS

VEHICLE	B.E.T. AREA	XRF Analysis (wt%) CATALYTIC COMPONENTS									
CATALYST	$(m^2/g)$	PT	RH	PD	NI	CE	BA	LA	FE	g/ft <sup>3</sup>	Pt/Pd/Rh
1988 3.0L Tau	rus	41,093	Miles					<del></del>	<del></del>	<del></del>	
MMT-BK4I	17.8	.1517	.0298	.0000	. 6795	6.0095	. 5896	.2234	. 3625	26.5	5.1/0/1.0
MMT-BK4M	20.6	.1745	.0367	.0000	. 6933	6.0214	. 6997	.2249	. 3584	30.8	4.8/0/1.0
MMT-BK40	18.6	.1909	.0408	.0000	. 6496	5.5291	.7712	.2060	.3794 Average:	33.8 30.4	4.7/0/1.0 4.8/0/1.0

VEHICLE	CONTAM	INATES						
CATALYST	PB	S	P	ZN	MN	CA	CL	CU
MMT-BK4I	.0788	.0000	.1340	.0675	1.0995	.0260	.0000	.0301
MMT-BK4M	.0262	.0000	.0792	.0197	. 5962	.0159	.0000	.0234
MMT-BK40	.0155	.0000	.0565	.0151	.4208	.0170	.0000	.0234

1988 3.0L Taurus- 41,093 Miles Inlet

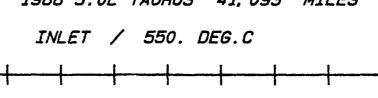


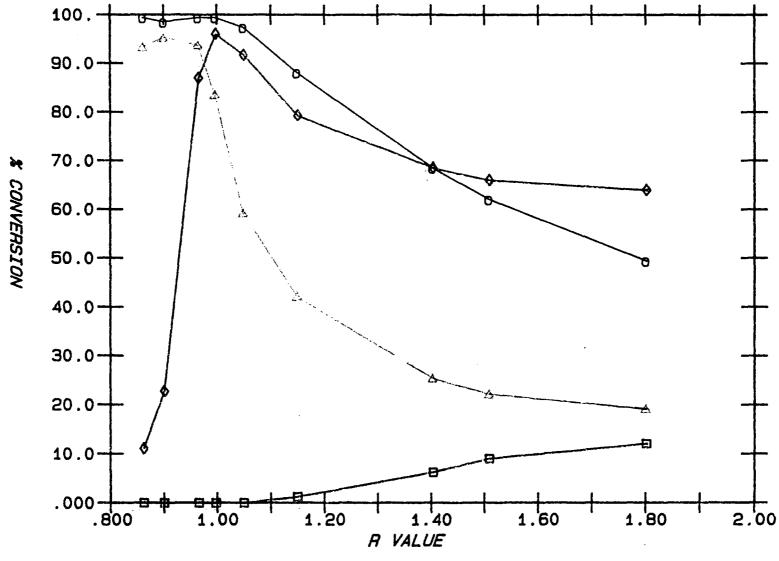


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 $\widetilde{\Sigma}$ 

45





4- HC 0 - CO

◊- NO □- NH3

xE 0

X O Appendix E 1988 3.0L Sable 21,500 Miles



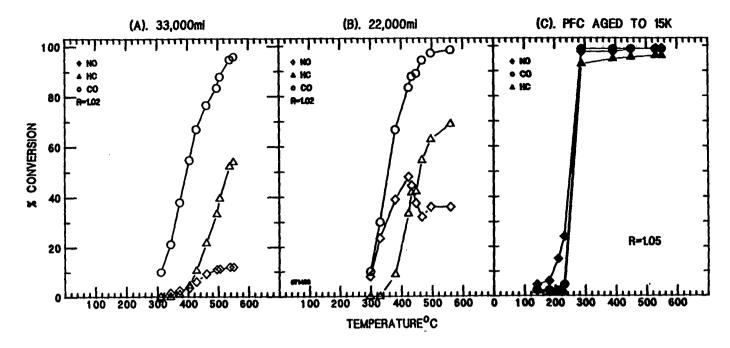


Figure 8. Comparison of the light-off NO, CO, and HC activities for (a) 33,000 miles MMT exposed catalyst, (b) 22,000 miles MMT exposed catalyst, and (c) 15,000 mile non-MMT pulsator aged catalyst.

channels of the converter. This plugging of the channels of the monolith results in an increase of the mass transfer resistance and consequently reduces the efficiency of the catalyst to convert HC, CO and  $\mathrm{NO}_{\mathrm{X}}.$  Based on these results it appears that the fuel additive MMT had a deleterious effect on the efficiency of the catalysts tested. However, in order to access more definitively the effect of MMT on in-use vehicle catalyst efficiency, this study suggests the need to correlate cause and effect from vehicles fueled with and without the fuel additive MMT.

#### **ACKNOWLEDGEMENTS**

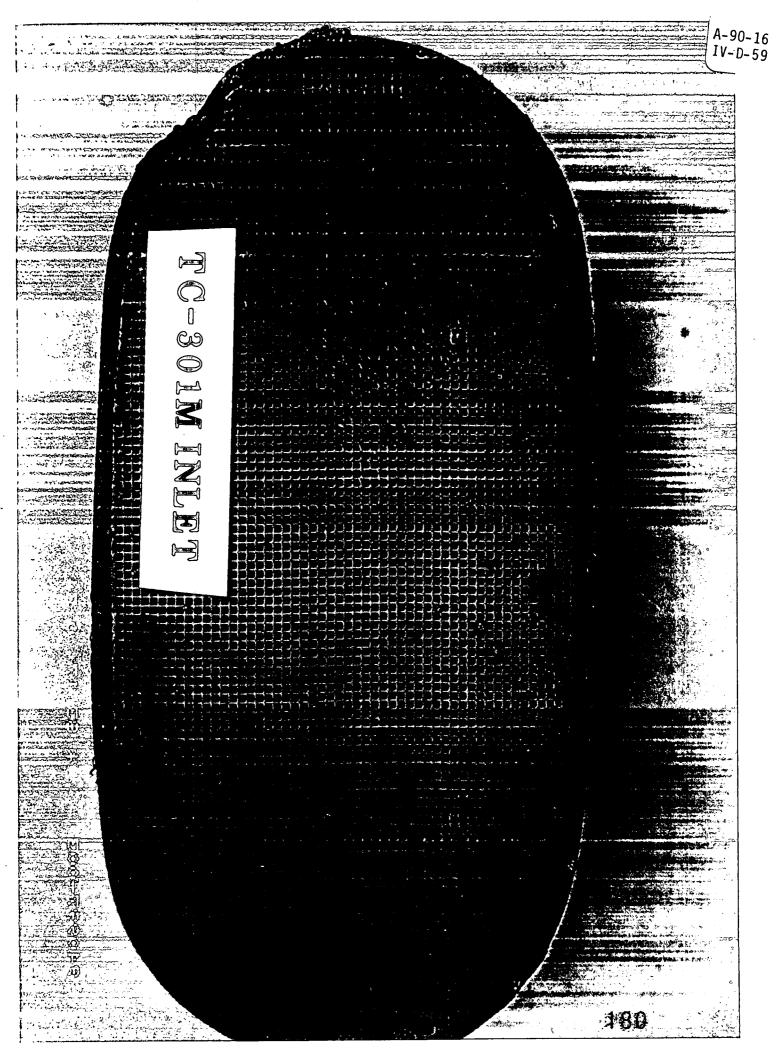
The authors gratefully acknowledge F. A. Alberts, W. Allie, Jr., R. K. Belitz, F. W. Kunz, and C. R. Peters who performed the many analytical analyses required by this characterization. The authors also acknowledge the helpful assistance of personnel from the Fleet Test Section, G. Bourdage, R. McCasland, L. Shannon, and D. Taylor and from Ford Canada Parts and Service, D. McIntosh and R. McTaggart. In addition, the authors acknowledge J. G. Thom and H. S. Gandhi who provided helpful criticism of the paper.

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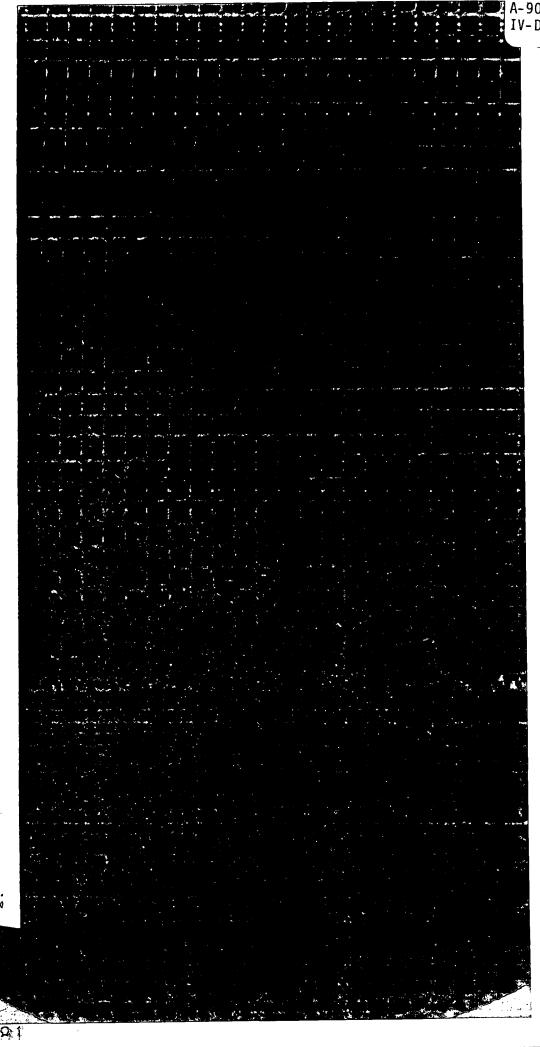
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A-90-16 IV-D-59

# 



## Effects-Of-MM-T-On

- Minor to severe clogging on inlet of catalysts from vehicles operated on MMT laden fuel
- Residue on inlets of catalysts confirmed to be Mn<sub>3</sub>O<sub>4</sub>, a combustion product of MMT
- Manganese concentration on inlets of first brick varies between 1.5% and 6.5% for vehicles having between 13,000 and 45,000 miles using MMT laden fuel
- The thickness of the Mn<sub>3</sub>O<sub>4</sub> layer on the washcoat varies between 5 and 30 microns for vehicles having between 13,000 and 45,000 miles using MMT laden fuel
- Catalysts efficiency for HC, CO, NO<sub>x</sub> emissions is reduced between 50 and 80% by the Mn<sub>3</sub>O<sub>4</sub> layer

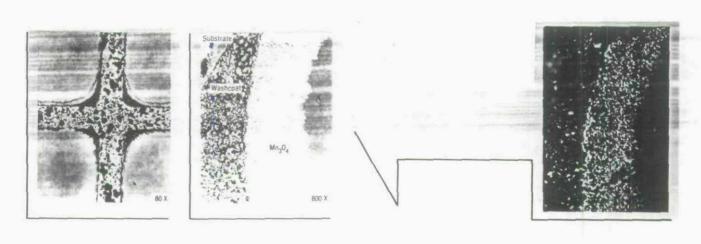
## Effects Of MMT-On Gatalysts

#### **Summary:**

- Catalyst efficiency deteriorates as exposure to MMT increases
- Mechanism of deactivation due to mass transfer resistance caused by Mn<sub>3</sub>O<sub>4</sub> buildup on washcoat surface
- Reported on effects of MMT at 1989
   International SAE Congress (SAE 890582)
- Discussed results with Ethyl, the EPA, and Ford-Canada
- Chrysler-Canada reported at SAE of experiencing similar problem with 40 of 200 catalysts
- Evaluating an additional 13 converters -25 catalysts (Total of 40 catalysts)
- Canadian MMT results have been forwarded to both Ford-Australia and to Ford-Europe

A-90-16 IV-D-59

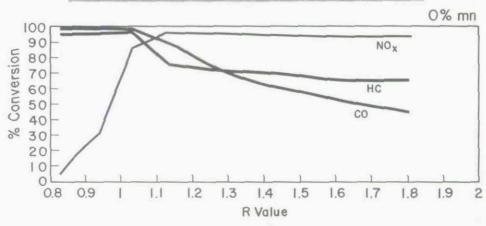
## **Effect Of MMT On Catalyst**



### Optical Micrograph of Catalyst (33,000 miles)

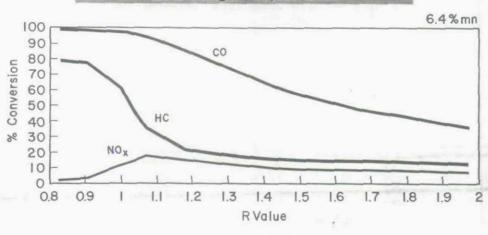
#### Catalyst Activity - Non MMT Fueled

3.0 L 86 Taurus 46,000 Miles



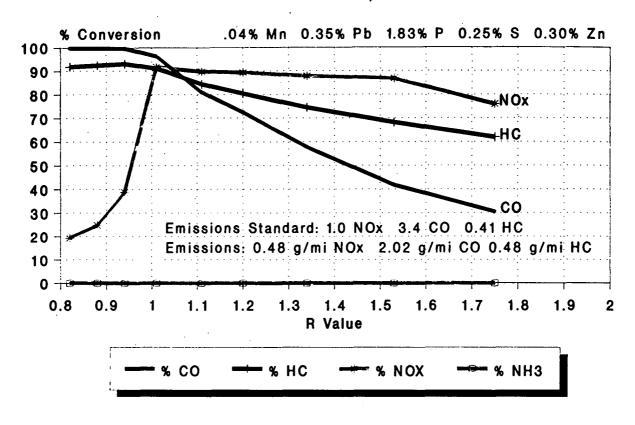
#### **Catalyst Activity - MMT Fueled**

2.3 L Ranger - 33,000 Miles

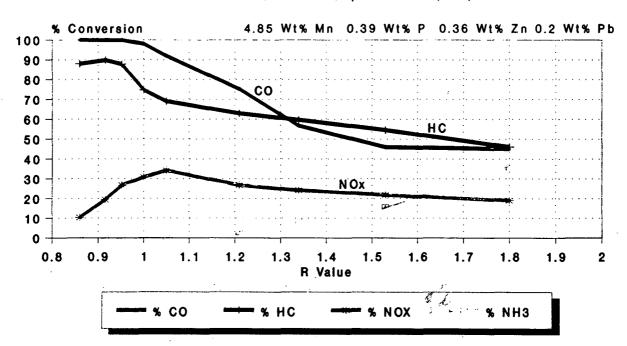


P.46

## Catalyst Activity - Non MMT Fueled 1.6L 83 Escort 38,792 miles



### Catalyst Activity - MMT Fueled 1.9L 86 Escort EFI 32,319 miles (104)



A-90-1

## Effects:Of-MM-T-On-Catalysts



1986 2.3L Topaz 23,744 Miles 1.4% Mn



1984 2.3L Ranger 32,879 Miles 6.1% Mn



1984 2.3L Ranger 32,879 Mlles 6.1% Mn



1985 2.3L Merkur 32,088 Miles 1.7% Mn

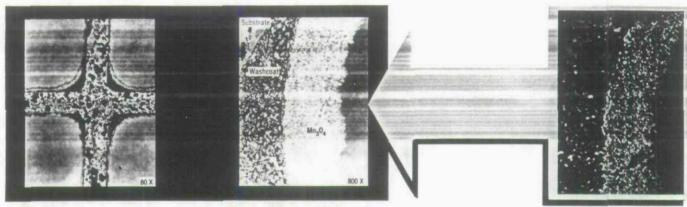


1987 5.8L LTD ( Police ) 58,000 Miles 5.1 % Mn

## Effect Of MMT On Catalyst

A-90-16 IV-D-59

### **Optical and SEM**

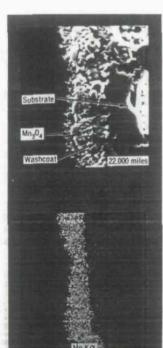


Optical Micrograph Of Catalyst ( 33,000 miles )

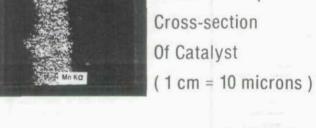


SEM
Micrographs —
Cross-section
Of Catalyst
( 1 cm = 10 microns )

Elemental Map -



SEM
Micrographs —
Cross-section
Of Catalyst
(1 cm = 10 microns)

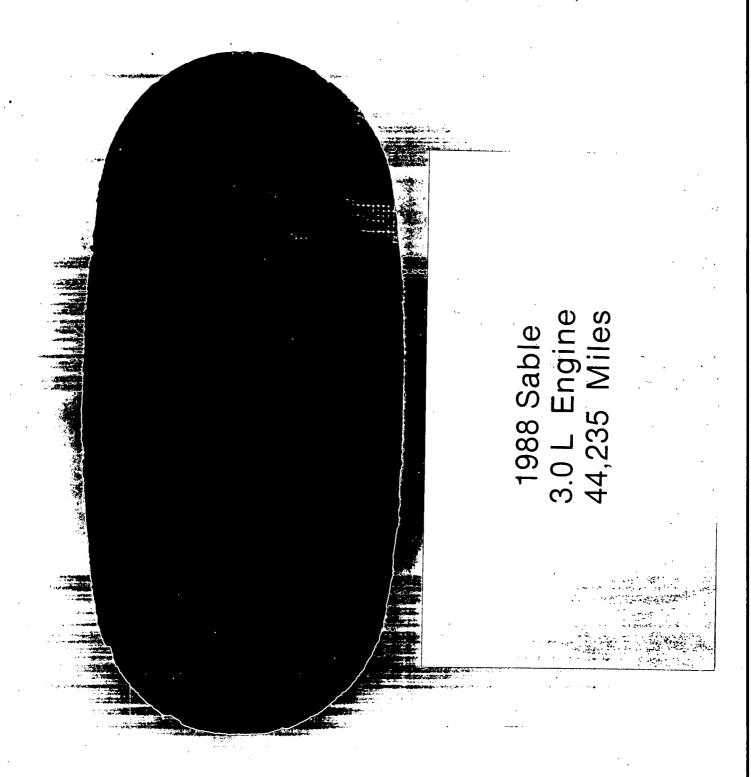


Mn

Mn
Elemental Map —
Cross-section
Of Catalyst
(1 cm = 10 microns)



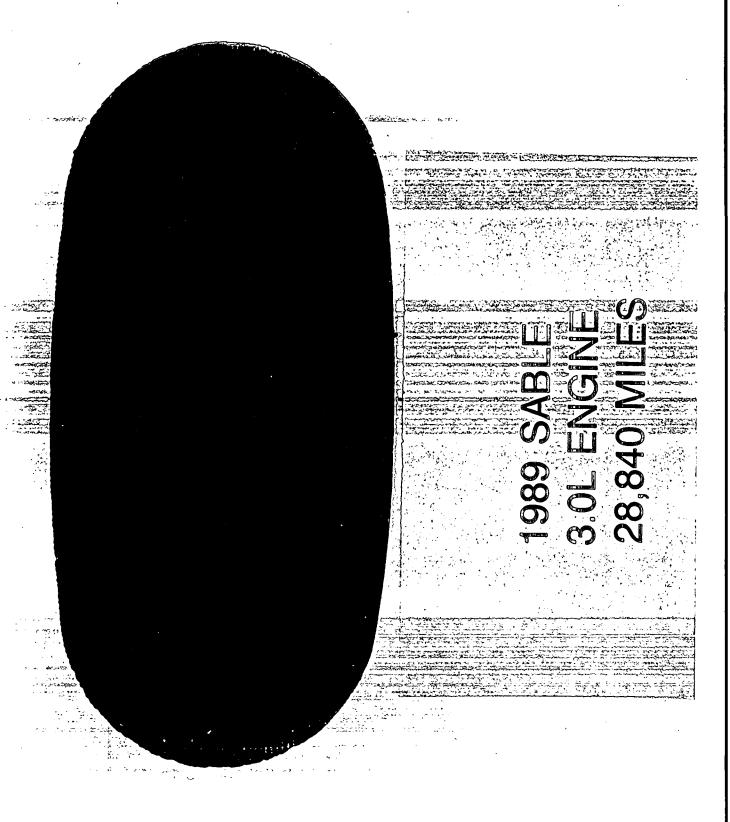
SEM
Photomicrograph
Of Surface Morphology
At 33,000 In-use Miles
( 1000 X )

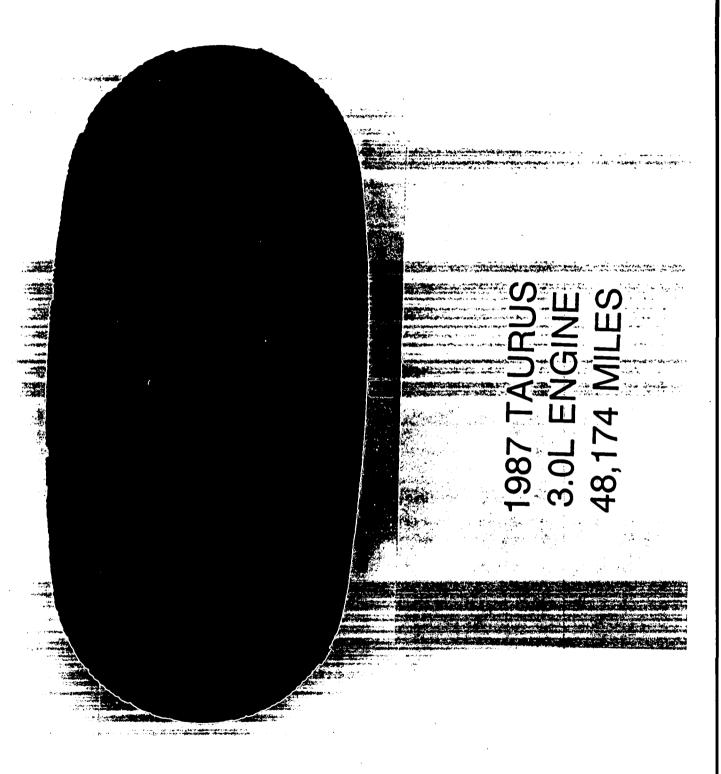


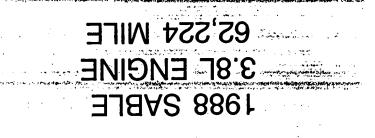
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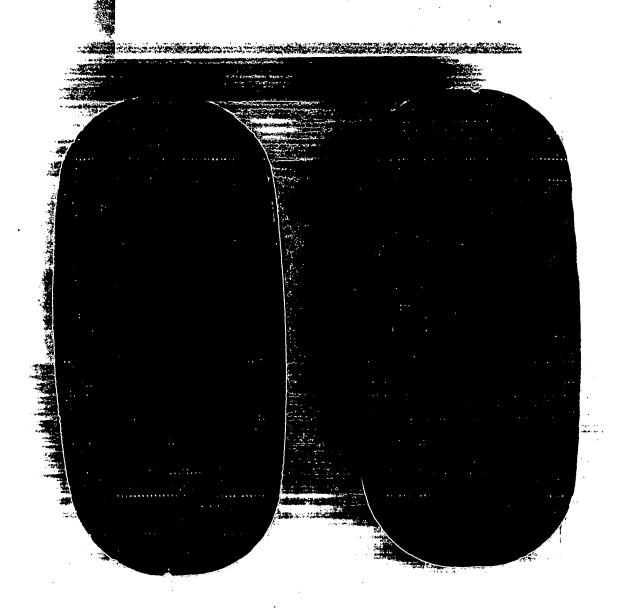
1988 TAURUS 3.0L ENGINE 35,733 MILES

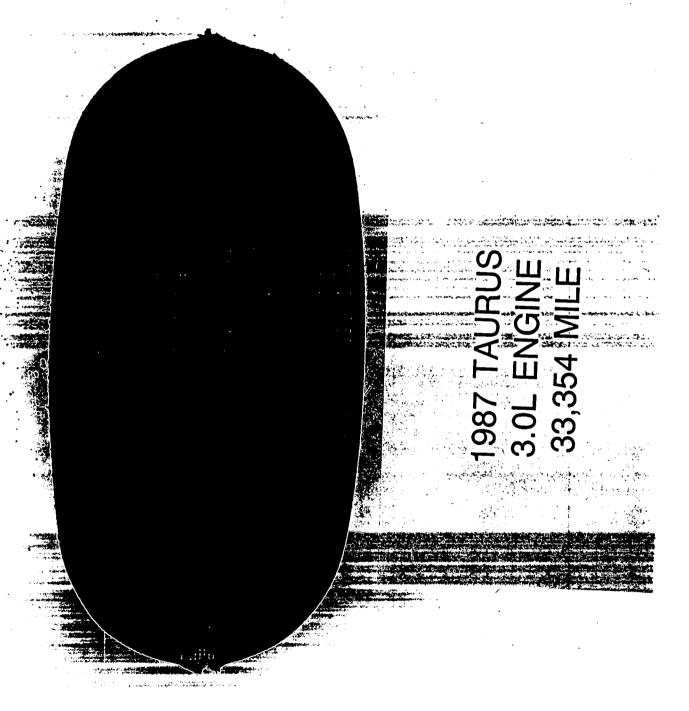
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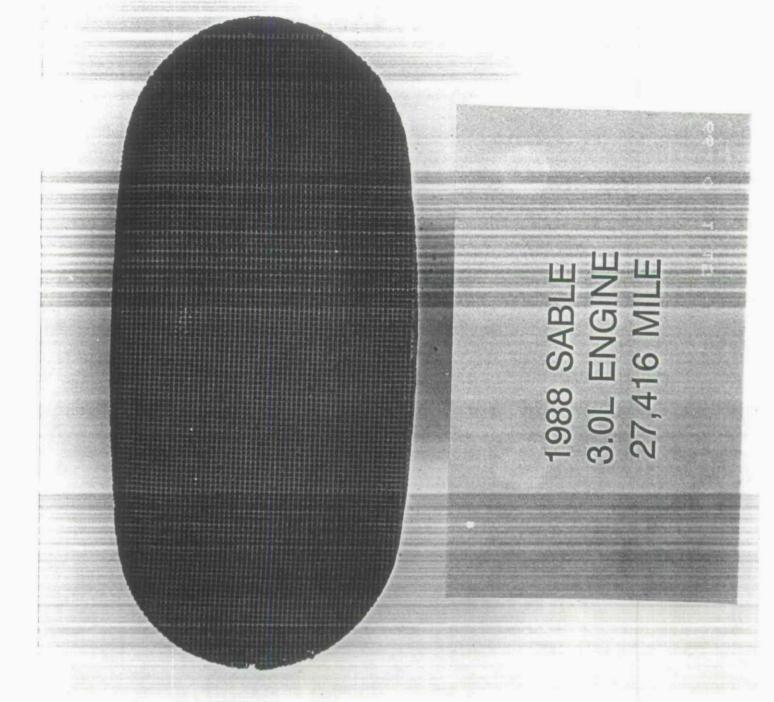


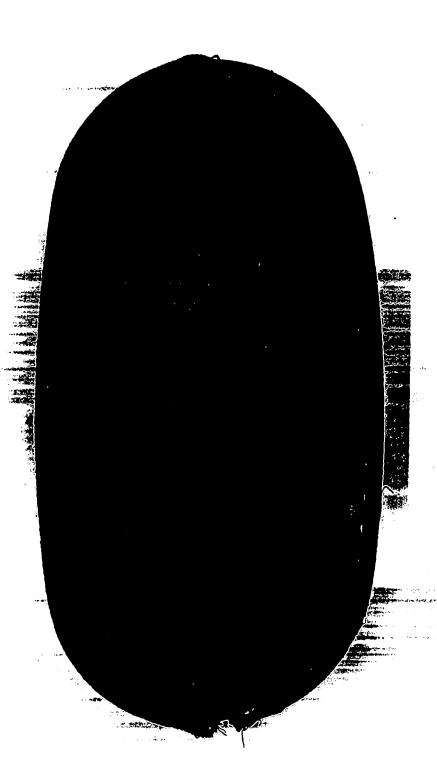












1988 TAURUS 3.0L ENGINE 39,662 MILE Paper Series



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## Results of Coordinating Research Council MMT Field Test Program



J. D. Benson
Fuels and Lubricants Department
General Motors Research Laboratories

R. J. Campion Exxon Company U.S.A.

L. J. Painter Chevron Research Company

Passenger Car Meeting Hyatt Regency, Dearborn June 11-15, 1979

SOCIETY OF AUTOMOTIVE ENGINEERS, INC. 400 COMMONWEALTH DRIVE WARRENDALE, PENNSYLVANIA 15096

## Results of Coordinating Research Council MMT Field Test Program

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SINCE 1975, MOST CARS PRODUCED IN THE U.S. have been equipped with catalytic converters for reducing exhaust emissions. These cars require the exclusive use of unleaded gasoline. As older cars are replaced by new, converterequipped cars, the demand for unleaded gasoline increases. To meet this demand and provide the desired octane quality, petroleum refiners in 1976 began using the fuel antiknock additive methylcyclopentadienyl manganese tricarbonyl (MMT) in unleaded gasoline. A prior study (1)\* and a review by the Environmental Protection Agency (2), had indicated that the use of MMT in unleaded gasoline did not adversely affect emissions, emission control systems, or other automotive components. The tests leading to these conclusions were carried out on vehicles equipped with first-generation oxidation catalysts; those vehicles were designed to meet the 1.5 g/mile hydrocarbon emission standard. As

\*Numbers in parentheses designate References at end of paper.

the use of MMT became more widespread, the EPA decided in 1977 (3) to include MMT in vehicle certification fuel for model year 1979. Concurrently, additional tests run by the automotive industry (4-5) had indicated that MMT increased hydrocarbon emissions and could, under some conditions, cause plugging of catalytic converters in advanced emission control systems. Thus, the automotive industry became concerned that they could not meet the 0.41 g/mile hydrocarbon standard as legislated for California in 1977 and nationwide by 1980.

The available data on MMT effects were reviewed extensively in early 1977, primarily at EPA-sponsored public meetings. These data from the automotive and petroleum industries and government laboratories were conflicting. To resolve this issue, the Coordinating Research Council (CRC), in mid-1977, undertook a comprehensive experimental program to determine whether MMT is detrimental to emission control in 1977-78 California vehicles. This cooperative CRC program was directed by technical representatives of the automotive and petroleum

- ABSTRACT .

The effect of the gasoline antiknock additive, MMT, on automotive emission control systems was studied in a 63-car field test. The cars were operated for 50 000 miles, and the effects of MMT on hydrocarbon, CO and NO $_{\rm X}$  emissions, catalyst plugging and spark plug life were determined.

Two concentration levels of MMT in a clear base fuel were studied, 1/32 g Mn/gal and 1/16 g Mn/gal. Seven 1977-78 model year cars, all calibrated to meet California standards, were included in the statistical design.

The results of this study indicate that the use of MMT at either test concentration increases both engine and tailpipe hydrocarbon emissions, compared to clear fuel. At 50K miles, the average tailpipe hydrocarbon increase was 0.09 g/mile for 1/32 MMT fuel, and 0.11 g/mile for 1/16 MMT fuel. This increase was pronounced at low mileage intervals, and significant differences continued for the duration of the test. CO and NO emissions, catalyst plugging, and spark plug life were not affected by MMT.

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industries, and included representatives of EPA and the California Air Resources Board as participating observers.

With the start of the CRC program, the EPA removed its requirement for the inclusion of MMT in certification fuel, pending completion of these tests. Also, in August of 1977, Congress passed and the President signed into law the Clean Air Act Amendments of 1977. These amendments included a ban of gasoline additives introduced after 1975 unless the EPA Administrator waived this prohibition under Section 211 of the Act. This ban was to be effective on September 15, 1978. Thus, the CRC program was aimed at providing both industries and the EPA with sound technical information upon which to judge the merits of the continued use of MMT. Ethyl Corporation, the sole manufacturer of MMT, applied for such a waiver in March of 1978.

To review all available data, EPA held a Public Hearing in June of 1978 on the Ethyl request. Although the CRC test was incomplete at that time, preliminary information obtained during 22 500 (22.5K) miles of testing was presented at the Public Hearing. In September 1978, the EPA Administrator rejected Ethyl's waiver request and a ban on the use of MMT in unleaded gasoline went into effect in October of 1978.

This paper presents the final results of the CRC program, which was probably the largest and most comprehensive test of its kind ever attempted. The program involved 63 cars which accumulated over 3 million miles. The primary objective was to determine the effect, relative to clear fuel, of MMT at two different concentration levels on exhaust hydrocarbon emissions. Secondary objectives were to determine MMT effects on catalytic converter plugging, catalyst conversion efficiency, oxygen sensor life, and spark plug life. All exhaust emission tests were conducted by Systems Control, Inc. (SCI) -- formerly Olson Laboratories -and the cars accumulated mileage at the Riverside International Raceway (RIR) under contract with SCI (6). A complete record of test details, experimental results, and data analysis can be obtained from the Coordinating Research Council (7).

#### EXPERIMENTAL PROGRAM

Because of the importance to both industries and the Nation of the continued use of MT, it was recognized at the outset that the accuracy and precision of the test results were critical to the program's goal. Small differences in already low exhaust emission levels would have to be determined with high statistical confidence. After consultation and review with the EPA, a fleet of 63 vehicles was chosen. This fleet size was designed to provide a statistically powerful test for detecting MMT-related emissions effects as small as a differ-

ence of approximately 0.1 g/mile hydrocarbon after 50K miles and/or a 40 percent difference in regression slopes<sup>2</sup>. Details of several approaches for estimating fleet size are included in the CRC Report (7).

The test design included the use of three fuels and seven vehicle models, six domestic and one foreign. All vehicles were designed to meet 1977-78 California exhaust emission standards. Three vehicles of each model were tested per fuel, resulting in a total of nine vehicles for each model. To involve the most advanced emission control systems available, two three-way catalyst equipped models were included. The six domestic models were divided among the three major U.S. manufacturers in approximate proportion to market share.

Vehicles selected by the car manufacturers for the fleet were those considered to be sensitive to MMT and/or representative of future large volume products. The vehicle fleet is described in Table 1.

Fuels selected for the program were Indolene clear (HO III) for emission testing and Chevron certification fuel for mileage accumulation. The Chevron fuel was tested clear (0 MMT), with 1/32 g. Mn/gal (1/32 MMT), and with 1/16 g Mn/gal (1/16 MMT). The 1/16 MMT level was selected because that was the maximum concentration recommended by Ethyl Corporation at the time this test program was finalized.

Originally, triplicate emission tests were conducted. Later it was decided, based on observed test precision, that duplicate emission tests were adequate at 0.3K, 5K, 10K, 15K, 22.5K, 30K, 37.5K, 45K, and 50K miles. Tests were run according to EPA exhaust emission certification procedures which includes preconditioning prior to emission testing, except that evaporative emission tests were not run. Scheduled maintenance was conducted at the manufacturer-recommended mileage. Emission testing at the maintenance intervals was conducted with each vehicle as received and after maintenance had been performed Maintenance procedures are discussed in a later section of this paper.

Vehicles accumulated mileage using the EPA driving schedule. Cars were driven a maximum of 19 hours per day. The vehicles were transported by car carriers between the laboratory and the test track, which were 50 miles apart.

An elaborate quality control and data management system was developed at the contracted laboratory, SCI, and at the test track, RIR. Before the program began, several CRC member companies assisted the SCI laboratory in setting up equipment, refining test procedures, and verifying test results to ensure that high quality emission test data would be obtained (6).

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<sup>\*</sup>Slope of the regression line for tailpipe HC emissions versus miles.

In addition, CRC hired a resident project manager and two full-time assistants to monitor the program on-site. This three-man staff was responsible only to CRC.

The CRC also formed a Data Analysis Panel composed of member-company representatives with extensive experience in emission measurements and statistical methods. This Panel is responsible for the data analyses included in this paper.

#### DATA ANALYSIS

ANALYTICAL METHODS - The data analysis was directed primarily at fuel effects on emission levels averaged over the full 50K miles of testing and at fuel effect changes as a function of test mileage.

Two different types of analyses were performed:

- Analysis of variance of emission levels, simultaneously accounting for fuel, mileage, and model effects.
- Regression analysis of emissions levels versus test miles to obtain linear rates of change of emissions with mileage which were subsequently analyzed to estimate fuel effects.

Each of these approaches makes a different use of the observed data base. Detailed descriptions of the analysis methods and the appropriate data sets are given in the CRC report (7).

DATA BASE - A complete listing of data from the 1801 valid Federal Test Procedure (FTP) tests is also given in the CRC Report (7). In this paper, these data are summarized primarily in the form of graphs.

Of the complete set of valid FTP data, only those tests meeting the following criteria were selected for use in the analyses:

- Data at scheduled test mileages, starting with 0.3K miles.
  - 2. Data after unscheduled maintenance.
- Data before and after scheduled maintenance.
  - 4. Data not involved in diagnostic checks.

A few sets of data were rejected because of obvious mechanical problems with the vehicles, such as a melted catalyst, a broken piston, or a malfunctioning carburetor.

TEST VARIABILITY - The test variabilities associated with duplicate and triplicate FTP tests and with the car to car differences were found to be within the estimates used in the design of the test program, assuring that the test as conducted was as powerful as originally planned.

Test Repeatability - The overall FTF test repeat error, defined as  $\hat{\sigma}$  (repeat) = standard deviation/mean x 100 percent, was 9.0 percent for tailpipe hydrocarbon (TPHC) and 5.2 percent for engine-out hydrocarbon (EOHC), based on over 1 100 degrees of freedom each. The car codels differed in their test repeatability for TPMC, falling into three groups as shown in

Table 2.

The engine-out HC precision shown in Table 2 does not exhibit any such strong grouping and does not correlate with the tailpipe precisions.

Car-Mileage Error - The car x mile error term from this program,  $\hat{\sigma}$  (car x miles), was 0.073 g/mile for tailpipe HC, giving 0.20 x  $10^{-5}$  g/mile/mile as the error for the difference between HC slope values for two fuels. These are slightly higher than, but within the uncertainty of the original estimates (0.056 g/mile and 0.15 x  $10^{-5}$  g/mile/mile) used to design the program (7).

The several car models form two definite groups with respect to the magnitude of this TPHC car x miles error term as shown in Table 3.

The original estimate of 0.056 g/mile is between the values found for the low and high error groups. No such groupings were found for the other emission constituents.

#### EXHAUST EMISSIONS

Exhaust emissions of hydrocarbons (HC). carbon monoxide (CO), and nitrogen oxides (NO,) were measured simultaneously at the engine ahead of the catalytic converter (engine-out) and at the tailpipe. Catalytic converter efficiencies were calculated from engine-out and tailpipe emission measurements. The effect of MMT on each of these emission constituents will be discussed in the following sections. For this discussion, data have been separated into three categories: 1) all car data; 2) data from all cars with conventional oxidation catalysts (COC) which includes the Buick Century, Oldsmobile Cutlass, Ford Granada, Ford LTD, and Plymouth Volare; and 3) data from cars with three-way catalysts (TWC) which includes the Pontiac Sunbirds and Volvos.

TAILPIPE HC EMISSIONS - Plots of tailpipe HC emissions from all cars, COC cars, and TWC cars are shown in Figures 1, 2, and 3, respectively. From these figures it is apparent that tailpipe HC emissions from the clear-fueled cars were consistently lower than emissions from the corresponding MMT-fueled cars throughout the 50K mile test. Furthermore, emissions with 1/32 MMT fuel were usually somewhat lower than those with 1/16 MMT fuel.

Another way to look at fuel effects is to plot the difference in tailpipe HC between MMT fuel and clear fuel at each mileage interval for each car group as is shown in Figures 4, 5, and 6. The MMT fuels averaged consistently higher tailpipe HC levels than did the clear fuel. As shown in Figure 4, the differences in emissions for MMT fuels compared to clear fuel increased linearly for the first 15K miles and then remained relatively constant at about 0.1 g/mile through 50K miles. At 15K miles the differences in tailpipe HC emissions for 1/32 MMT compared to clear fuel was 0.09 g/mile and the difference for 1/16 MMT compared to

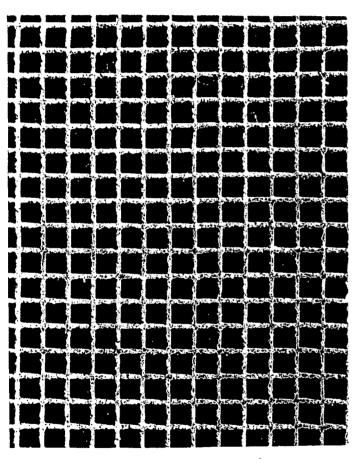
#### X-RAY FLUORESCENCE ANALYSIS OF MMT CATALYSTS

VEHICLE	B.E.T. AREA	XRF Analysis (wt%) CATALYTIC COMPONENTS									
CATALYST	$(m^2/g)$	PT	RH	PD	NI	CE	BA	LA	FE	g/ft <sup>3</sup>	Pt/Pd/Rh
1988 3.0L Sable		21,500	Miles			····		<u> </u>			
MMT-BK5I	15.9	.1838	.0397	.0000	. 7859	6.3163	.7197	. 2434	.4262	32.6	4.6/0/1.0
MMT-BK5M	13.6	.1896	.0412	.0000	. 8266	6.4745	.7607	. 2458	.4168	33.7	4.6/0/1.0
MMT-BK50	13.5	.2012	.0448	.0000	.8219	6.2063	.8177	.2339	.4204	35.9	4.5/0/1.0
									Average:	34.1	4.6/0/1.0

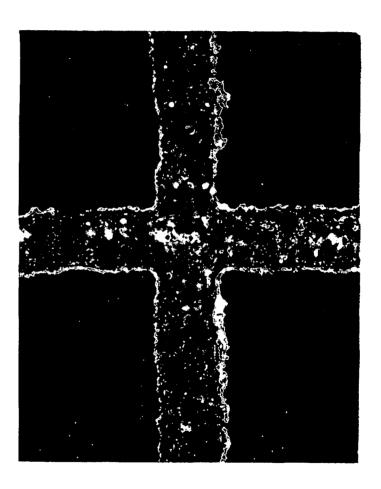
CONTAMINATES	CO	NTA	MTN	ልጥፑና
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VEHICLE								
CATALYST	PB	S	P	ZN	MN	CA	CL	CU
MMT-BK5I	.0387	.0435	.0959	.0460	.9464	.0150	.0000	.0268
MMT-BK5M	.0166	.0347	.0503	.0082	.4242	.0092	.0066	.0232
MMT-BK50	.0137	.0332	.0358	.0063	.2913	.0095	.0316	.0234

## 1988 3.0L Sable- 21,500 Miles Inlet







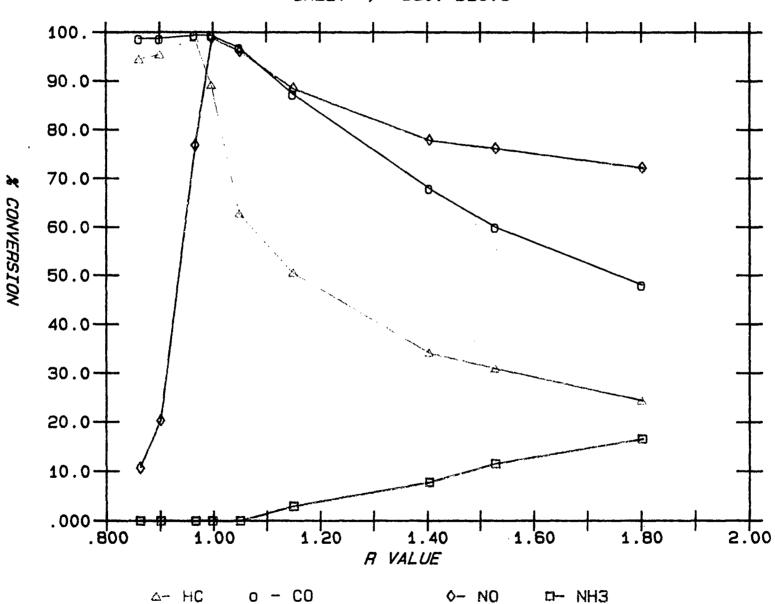
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MMT #5 1988 3.0L SABLE 21,500 MILES

INLET / 550. DEG.C

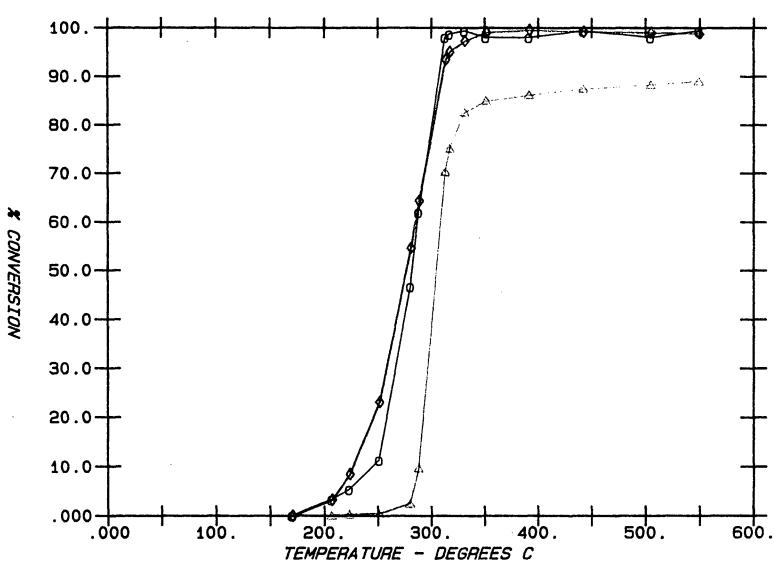


△- HC

0- NO

CHN -CI





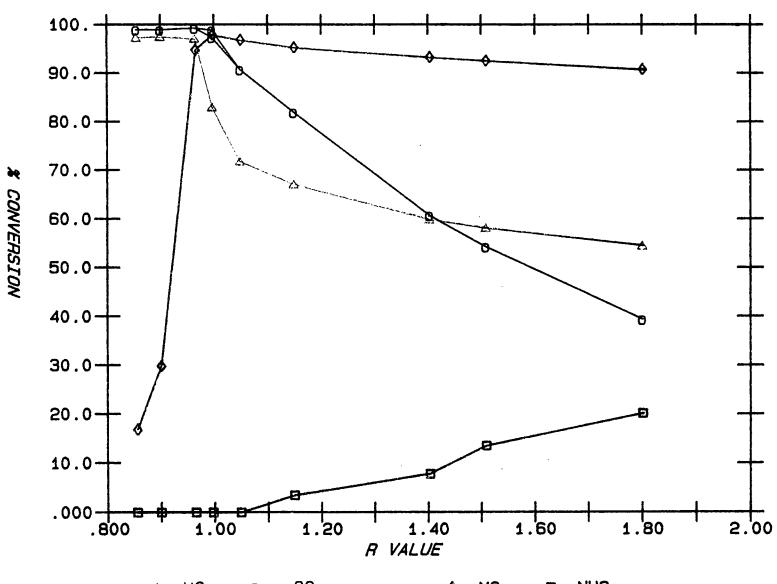
Δ- HC

o - CO

0- NO

52

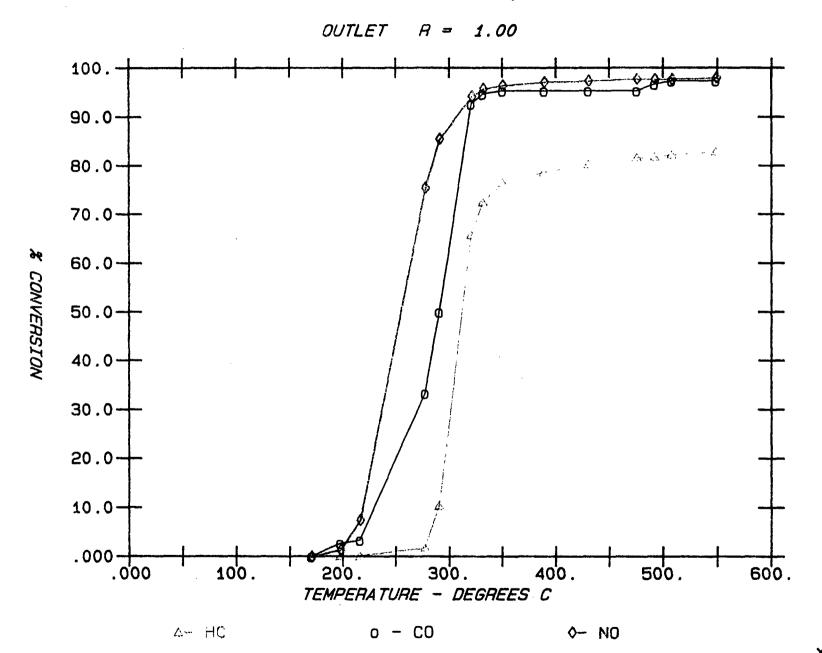




△- HC o - CO

♦— NO □— NH3



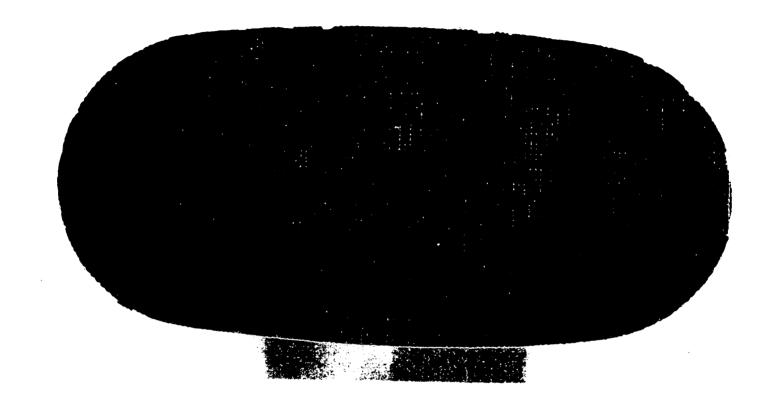


Appendix F 1987 3.0L Taurus 48,174 Miles

#### X-RAY FLUORESCENCE ANALYSIS OF MMT CATALYSTS

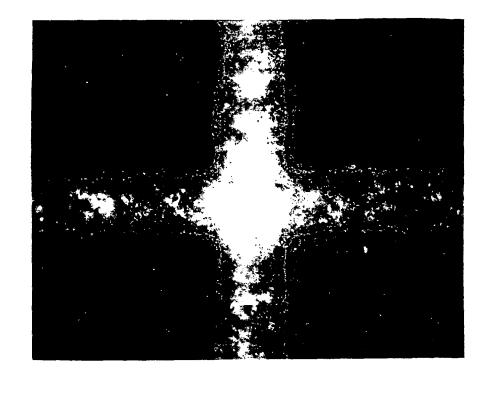
VEHICLE	B.E.T. AREA	XRF Analysis (wt%) CATALYTIC COMPONENTS									
CATALYST	$(m^2/g)$	PT	RH	PD	NI	CE	BA	LA	FE	g/ft <sup>3</sup>	Pt/Pd/Rh
1987 3.0L Taur	au au	48,174	Miles	<del></del>	<del></del>			,			
MMT-BK6I	16.9	.1058	. 0208	.0000	.7835 6	.5841	. 7865	. 2452	.4071	18.5	5.1/0/1.0
MMT-BK6M	17.9	.1068	.0219	.0000	.8256 6	.8790	.8273	. 2593	. 3606	18.8	4.9/0/1.0
MMT-BK60	18.7	.1025	.0203	.0000	.8445 6	.9089	.7971	.2602	.3644 Average:	17.9 18.4	5.0/0/1.0 5.0/0/1.0

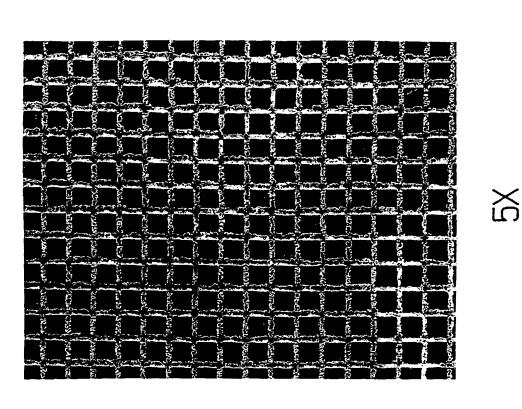
VEHICLE	CONTAMINATES								
CATALYST	PB	S	P	ZN	MN	CA	CL	CU	
MMT-BK6I	.1295	.0709	.1247	.0910	1.7447	.0859	.0000	.0241	
MMT-BK6M	.0378	.0184	.0720	.0253	.9720	.0210	.0000	.0286	
MMT-BK60	.0242	.0067	.0555	.0163	.6614	.0179	.0000	.0213	



1987 TAURUS 3.0L ENGINE 48,174 MILES

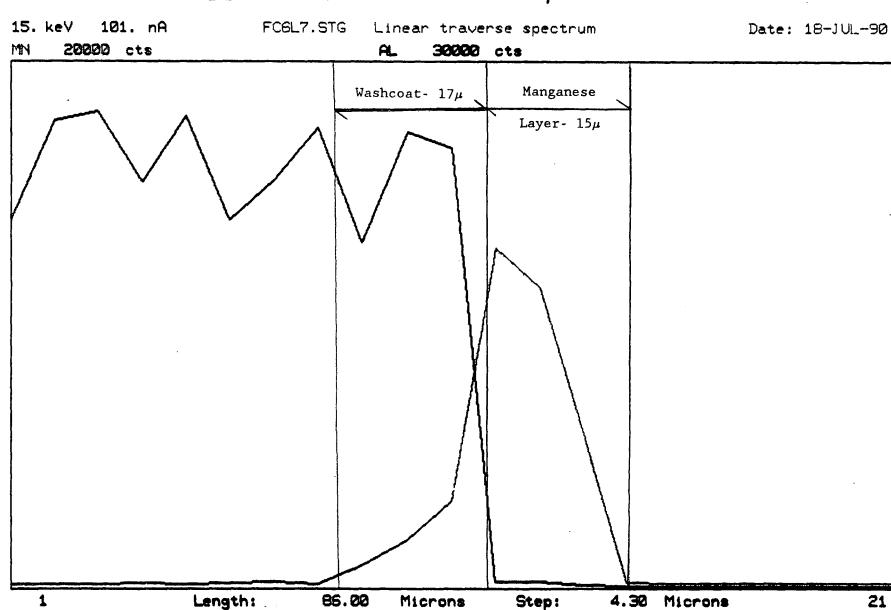
1987 3.0L Taurus- 48,174 Miles Inlet





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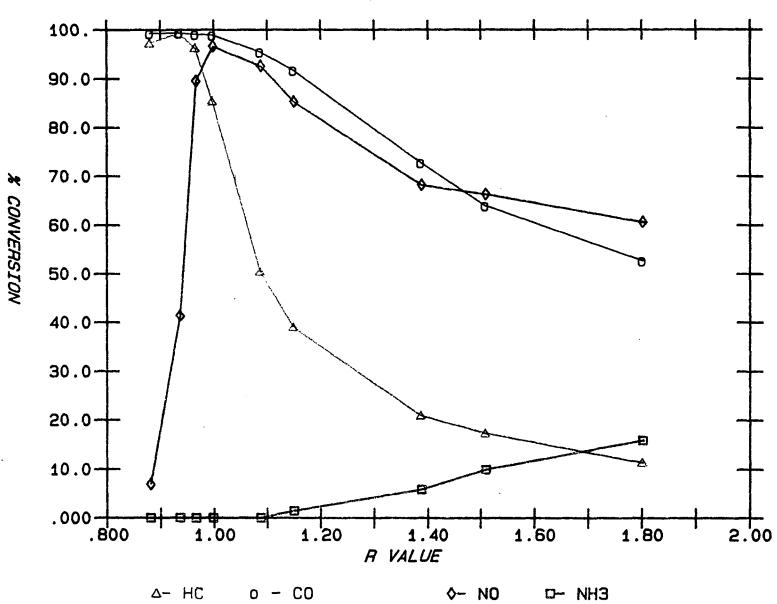
## 1987 3.0L Taurus- 48,174 Miles

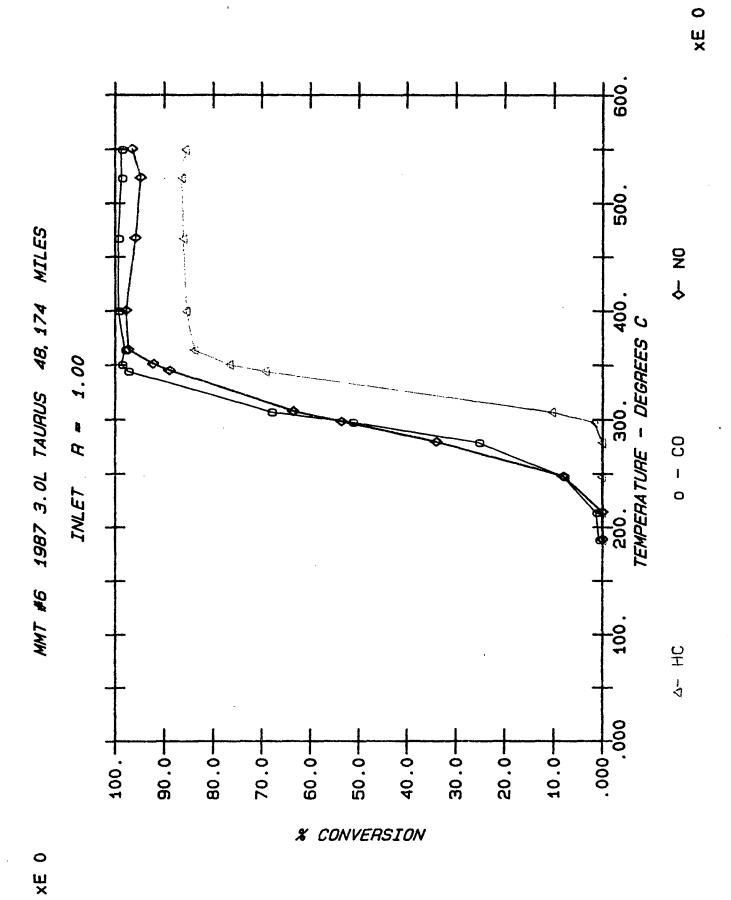


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INLET / 550. DEG.C





Appendix G 1988 3.8L Sable 62,224 Miles

VEHICLE	B.E.T. AREA		nalysis TIC COM	(wt%) IPONENTS	l					
CATALYST	$(m^2/g)$	PT	RH	PD	NI CE	BA	LA	FE	g/ft <sup>3</sup>	Pt/Pd/Rh
1988 3.8L Sable	<del></del>	62,224						<del></del>		
MMT-BK7BI	17.5	. 1297	.0256	.0000	.8338 6.575	1 .8236	.2611	.3293	22.7	5.1/0/1.0
MMT-BK7BM	10.1	.1109	.0245	.0000	.7357 6.163	8 .7311	.2439	.3410	19.8	4.5/0/1.0
MMT-BK7BO	8.4	.1163	.0259	.0000	.7354 6.350	2 .8279	.2571	.3498	20.8	4.5/0/1.0
					•			Average:	21.1	4.7/0/1.0

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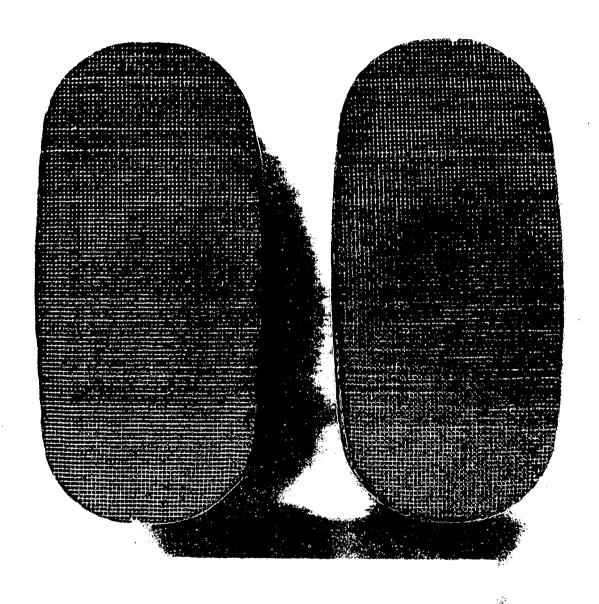
VEHICLE							
CATALYST	РВ	S	P	ZN MN	CA	CL	CU
MMT-BK7BI	.1564	.0000	.2588	.3012 3.2341	.0478	.0000	.0314
MMT-BK7BM	.0476	.0000	.1422	.0892 1.8793	.0207	.0000	.0219
MMT-BK7BO	.0306	.0000	.1461	.0908 1.8992	.0304	.0000	.0206

VEHICLE	B.E.T. AREA		nalysis TIC COM	(wt%) PONENTS							
CATALYST	$(m^2/g)$	PT	RH	PD	NI	CE	BA	LA	FE	g/ft <sup>3</sup>	Pt/Pd/Rh
1988 3.8L Sable		62,224	Miles								
MMT-BK7AI	21.6	.1434	.0306	.0000	.6992	5.7912	.7650	.2309	. 2985	25.4	4.7/0/1.0
MMT-BK7AM	19.7	.1317	.0281	.0000	.6584	5.6960	.7249	.2212	. 2949	23.3	4.7/0/1.0
MMT-BK7AO	17.7	.1236	.0268	.0000	. 6037	5.3997	. 6719	. 2085	.2970 Average:	21.9 23.6	4.6/0/1.0 4.7/0/1.0

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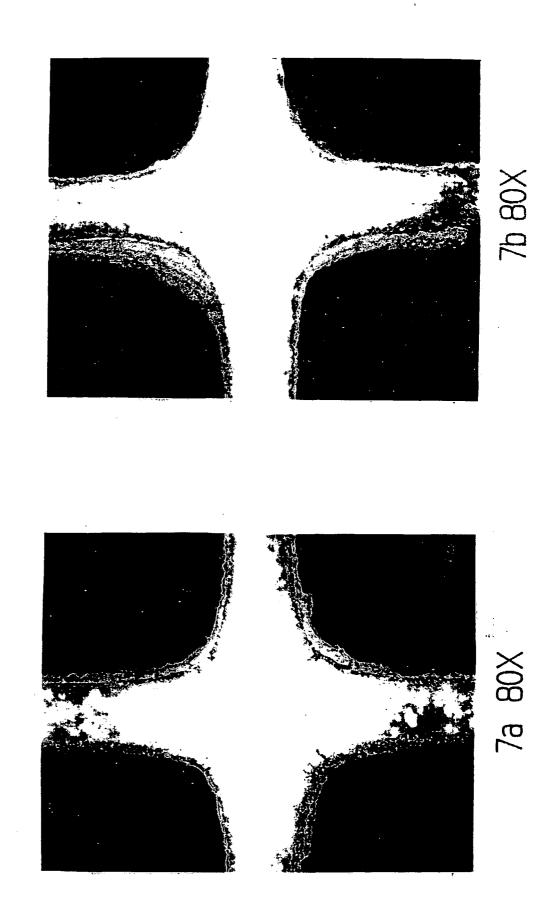
#### CONTAMINATES

VEHICLE								
CATALYST	PB	S	P	ZN	MN	CA	CL	CU
MMT-BK7AI	.1785	.0000	.2079	. 2091	2.0725	.0197	.0000	.0302
MMT-BK7AM	.0885	.0000	.1106	.0714	.9682	.0015	.0000	.0257
MMT-BK7AO	.0860	.0000	.0971	.0481	.9481	.0056	.0000	.0240

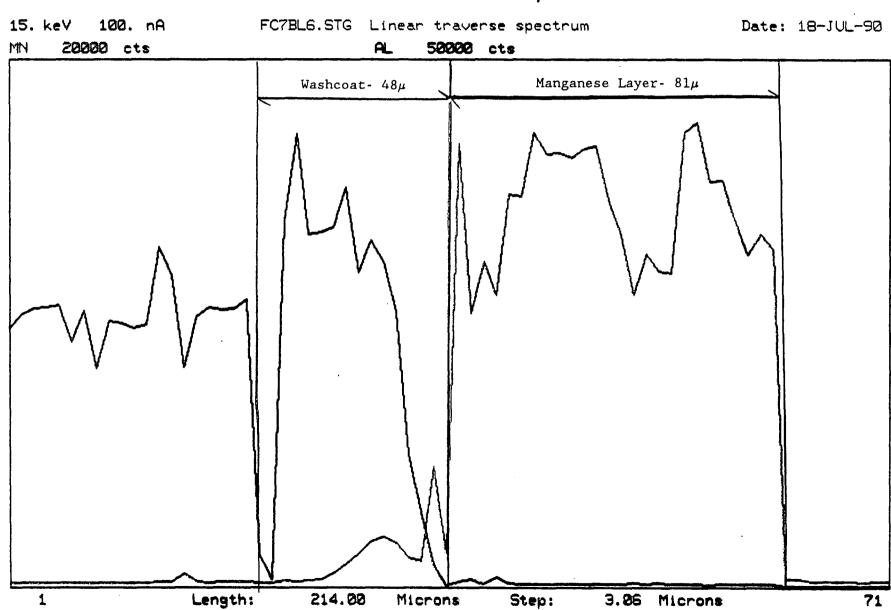


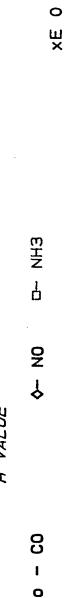
1988 SABLE 3.8L ENGINE 62,224 MILE

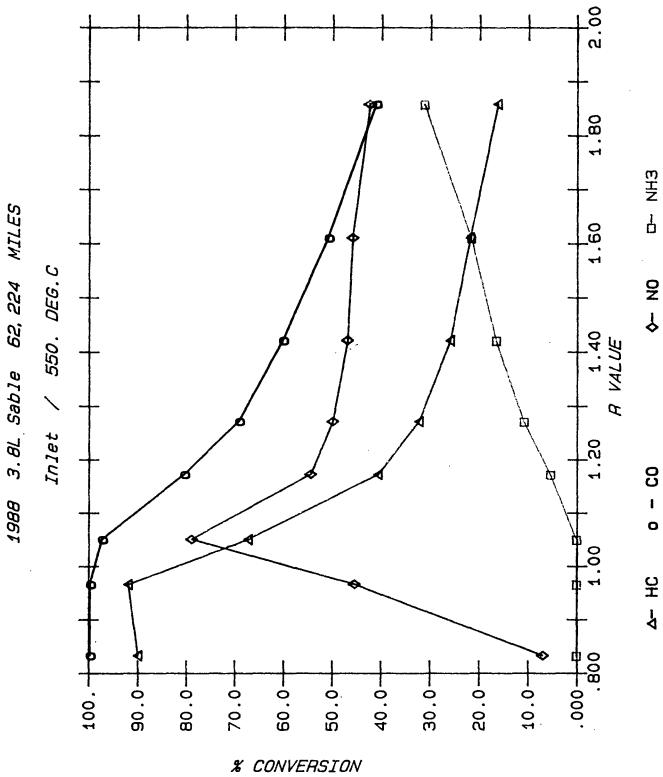
1988 3.8L Sable- 62,224 Miles Inlet



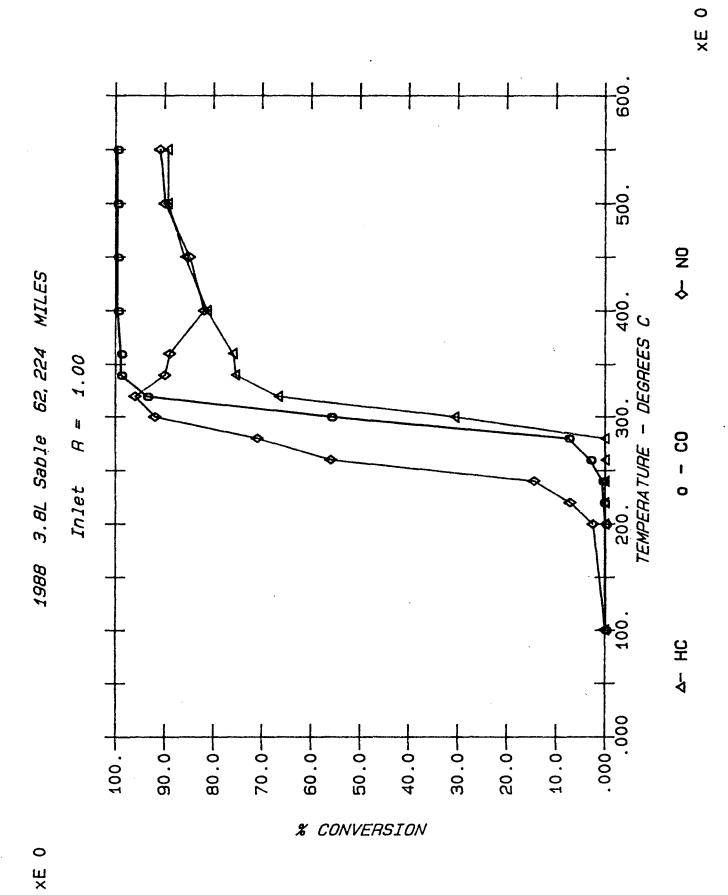
# 1988 3.8L Sable- 62,224 Miles



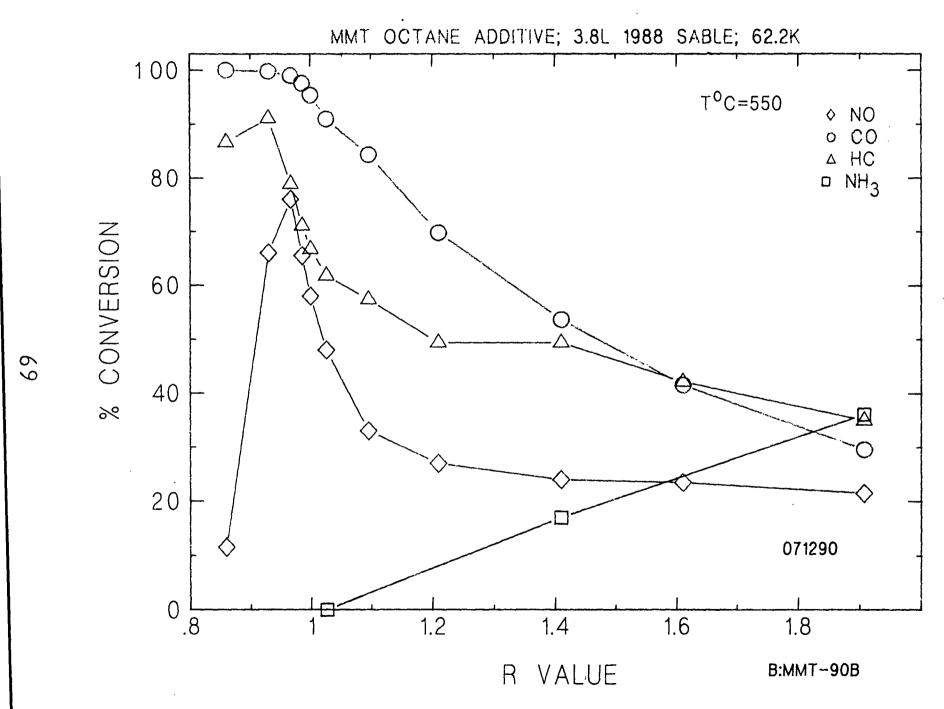


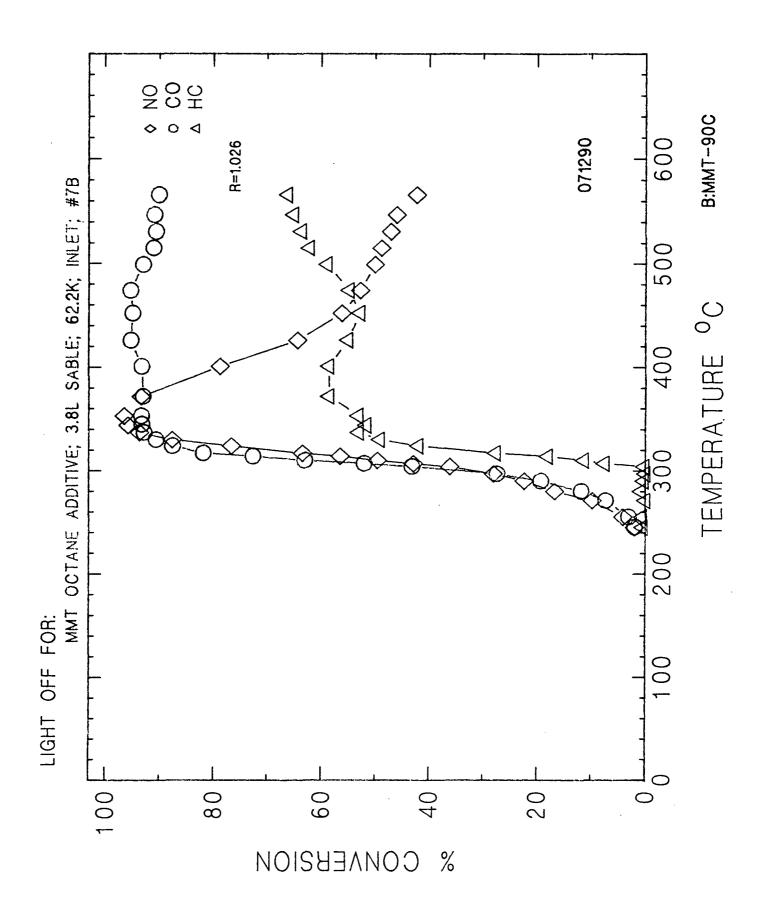


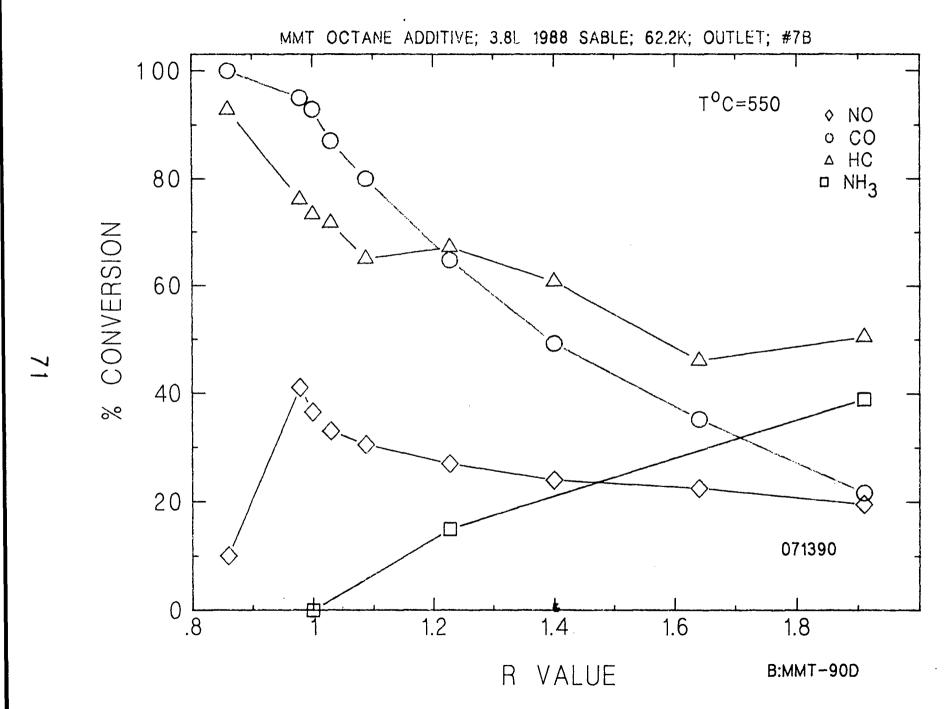
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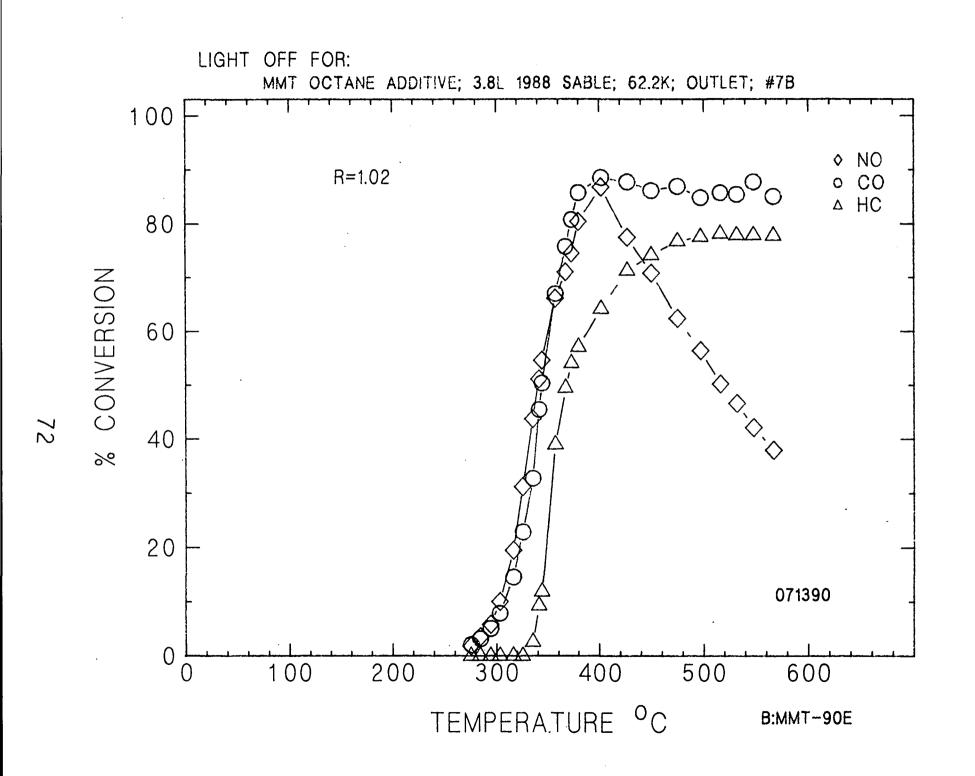


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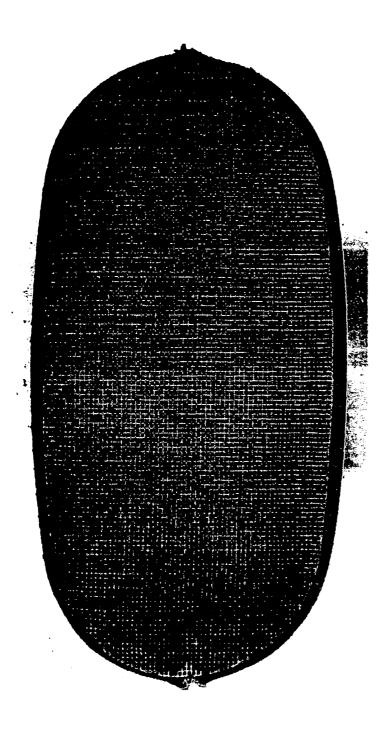


Appendix H 1987 3.0L Taurus 33,354 Miles

VEHICLE	B.E.T. AREA		nalysis TIC COM	(wt%) PONENTS	<u> </u>						
CATALYST	$(m^2/g)$	PT	ŖH	PD	NI	CE	BA	LA	FE	g/ft <sup>3</sup>	Pt/Pd/Rh
1987 3.0L Taux	rus	33,354	Miles		·						-
MMT-BK8I	16.6	.0957	.0195	.0000	.6430	6.3581	.7382	.2752	. 3026	16.8	4.9/0/1.0
MMT-BK8M	18.1	.0992	.0206	.0000	. 6835	6.5212	.7867	.2775	.2614	17.5	4.8/0/1.0
MMT-BK80	15.0	.1000	.0191	.0000	.6737	6.3627	.7749	.2711	.2661	17.4	5.2/0/1.0
									Average:	17.2	5.0/0/1.0

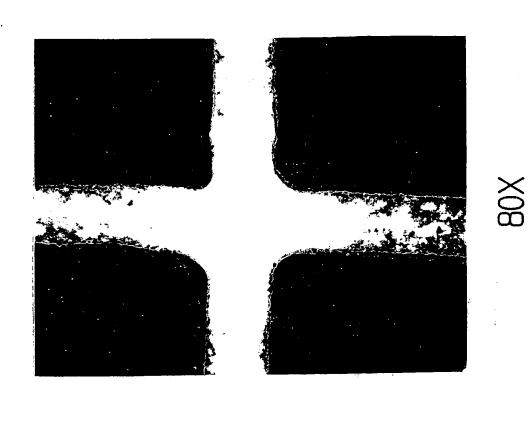
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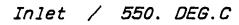
VEHICLE					•			
CATALYST	PB	S	P	ZN	MN	CA	CL	cu
MMT-BK8I	.2153	.0594	.1569	.1083	1.2705	.0532	.0000	.0310
MMT-BK8M	.0673	.0314	.0779	.0270	.5982	.0093	.0000	.0264
MMT-BK80	.0453	.0463	.0648	.0184	.4806	.0084	.0000	.0248

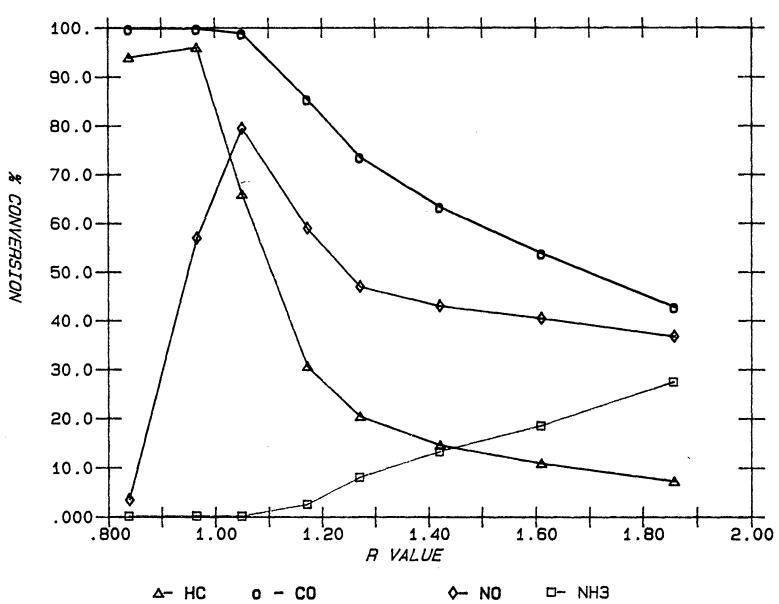


1987 TAURUS 3.0L ENGINE 33,354 MILE

1987 3.0L Taurus- 33,354 Miles Inlet

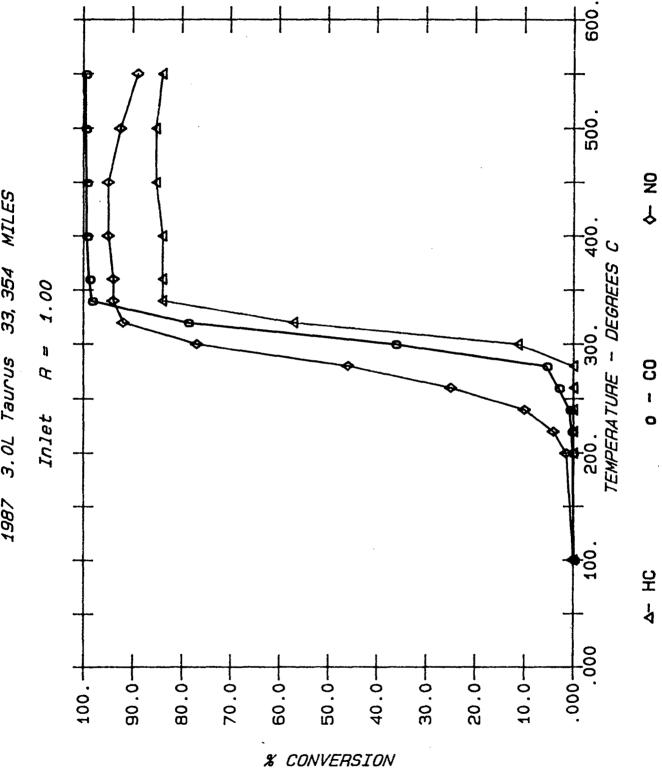






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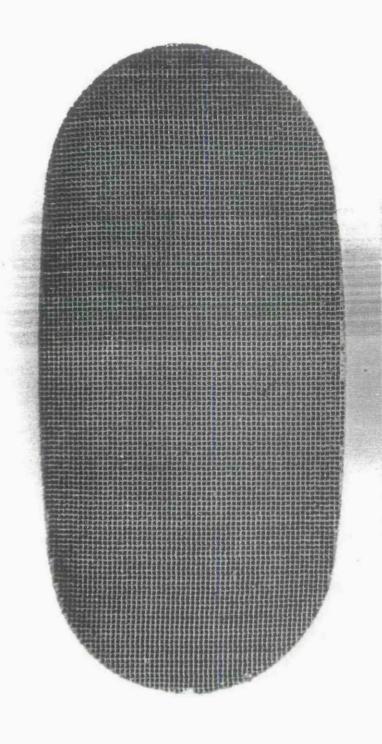
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Appendix I 1988 3.0L Sable 27,416 Miles

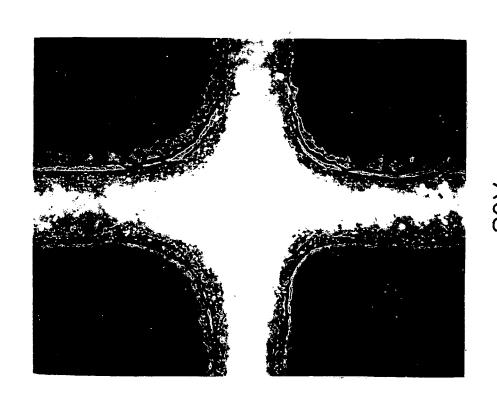
VEHICLE	B.E.T. AREA		nalysis TIC COM	(wt%)							·
CATALYST	$(m^2/g)$	PT	RH	PD	NI	CE	BA	LA	FE	g/ft <sup>3</sup>	Pt/Pd/Rh
1988 3.0L Sa	able	27,416	Miles								
MMT-BK9I	19.2	. 2302	.0463	.0000	.8121	5.4610	.8382	. 2047	. 3127	40.4	5.0/0/1.0
MMT-BK9M	19.1	.1943	.0391	.0000	.7457	5.3560	.7030	.2018	. 2926	34.4	5.0/0/1.0
MMT-BK90	19.9	.1964	.0386	.0000	.7443	5.3895	. 8043	.2022	.3113	34.3	5.1/0/1.0
									Average:	36.2	5.0/0/1.0

80	VEHICLE	CONTAMINATES									
	CATALYST	PB	S	P	ZN	MN	CA	CL	CU		
	MMT-BK9I	.1215	.0000	.2145	.1476	.9821	.0114	.0000	.0325		
	MMT-BK9M	.0649	.0000	.0907	.0302	.5311	.0041	.0000	.0249		
	MMT_REQO	0505	0000	(1602	0178	4021	በበጸበ	0000	0241		



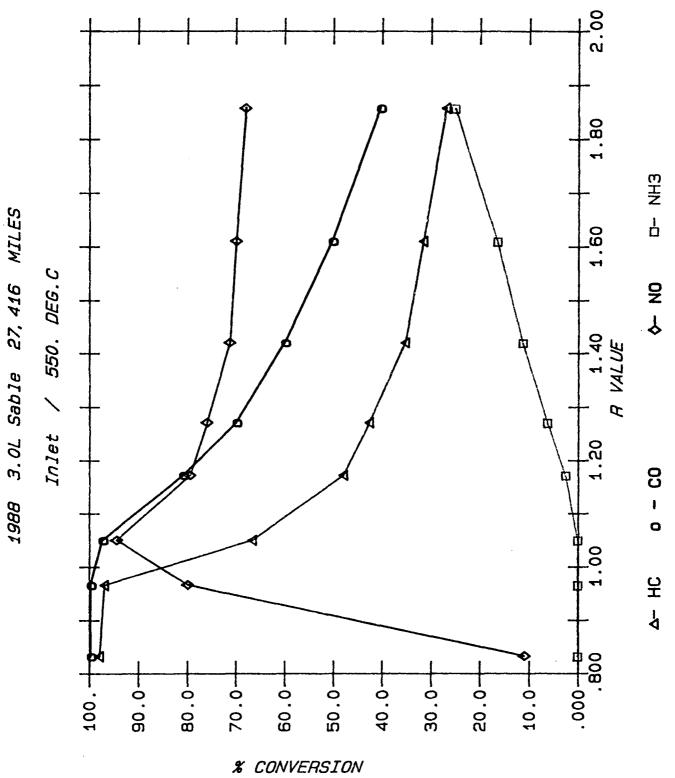
1988 SABLE 3.0L ENGINE 27,416 MILE

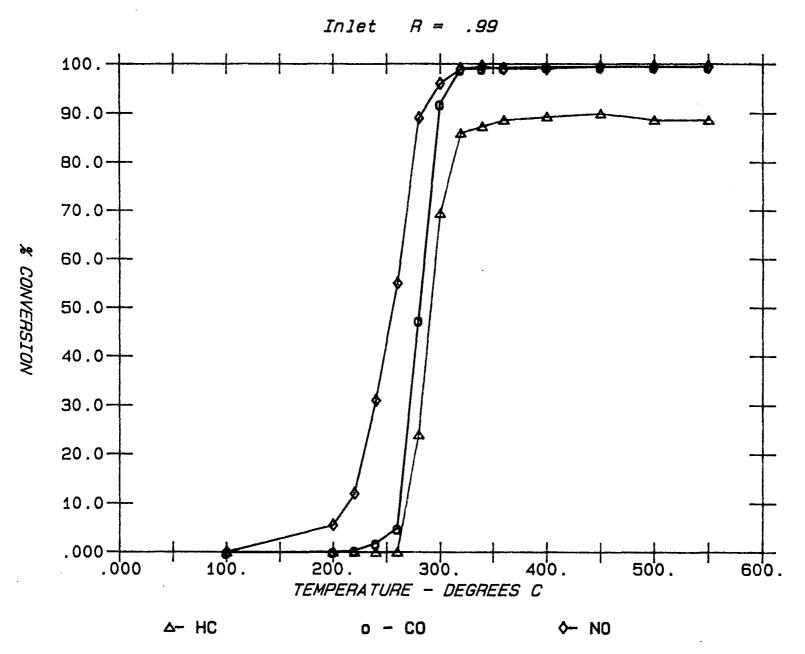
1988 3.0L Sable- 27,416 Miles Inlet



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Appendix J 1988 3.0L Taurus 39,662 Miles

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VEHICLE	B.E.T. AREA	XRF Analysis (wt%) CATALYTIC COMPONENTS									
CATALYST	$(m^2/g)$	PT	RH	PD	NI	CE	BA	LA	FE	g/ft <sup>3</sup>	Pt/Pd/Rh
1988 3.0L Ta	urus	39,662	Miles								
MMT-BK10I	21.9	. 2083	.0415	.0000	.7752 5	5.5875	.7679	.2161	. 2927	36.5	5.0/0/1.0
MMT-BK10M	18.8	. 1904	.0381	.0000	.7462 5	5.6083	.6995	.2183	. 2898	33.4	5.0/0/1.0
MMT-BK100	17.2	.1910	.0371	.0000	.7109 5	5.6701	.7052	.2248	. 2905	33.3	5.1/0/1.0
									Average:	34.4	5.0/0/1.0

VEHICLE	CONTAMINATES										
CATALYST	PB	S	P	ZN	MN	CA	CL	CU			
MMT-10I	.1262	.1277	.0818	.0888	.7912	.0077	.0000	.0242			
MMT-10M	.0309	.0964				.0000	.0000	.0222			
MMT-100	.0180	.0683	.0413	.0141	. 4419	. 0000	. 0000	.0221			